

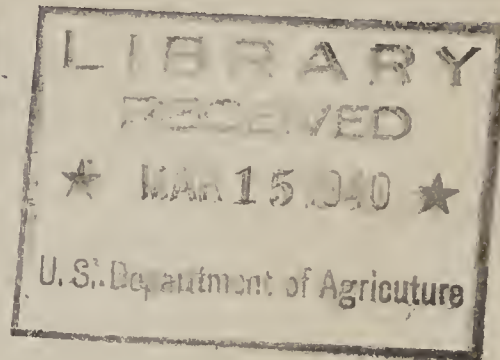
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**METHODS USED AT THE FOREST PRODUCTS LABORATORY
FOR THE CHEMICAL ANALYSIS OF PULPS
AND PULPWOODS**

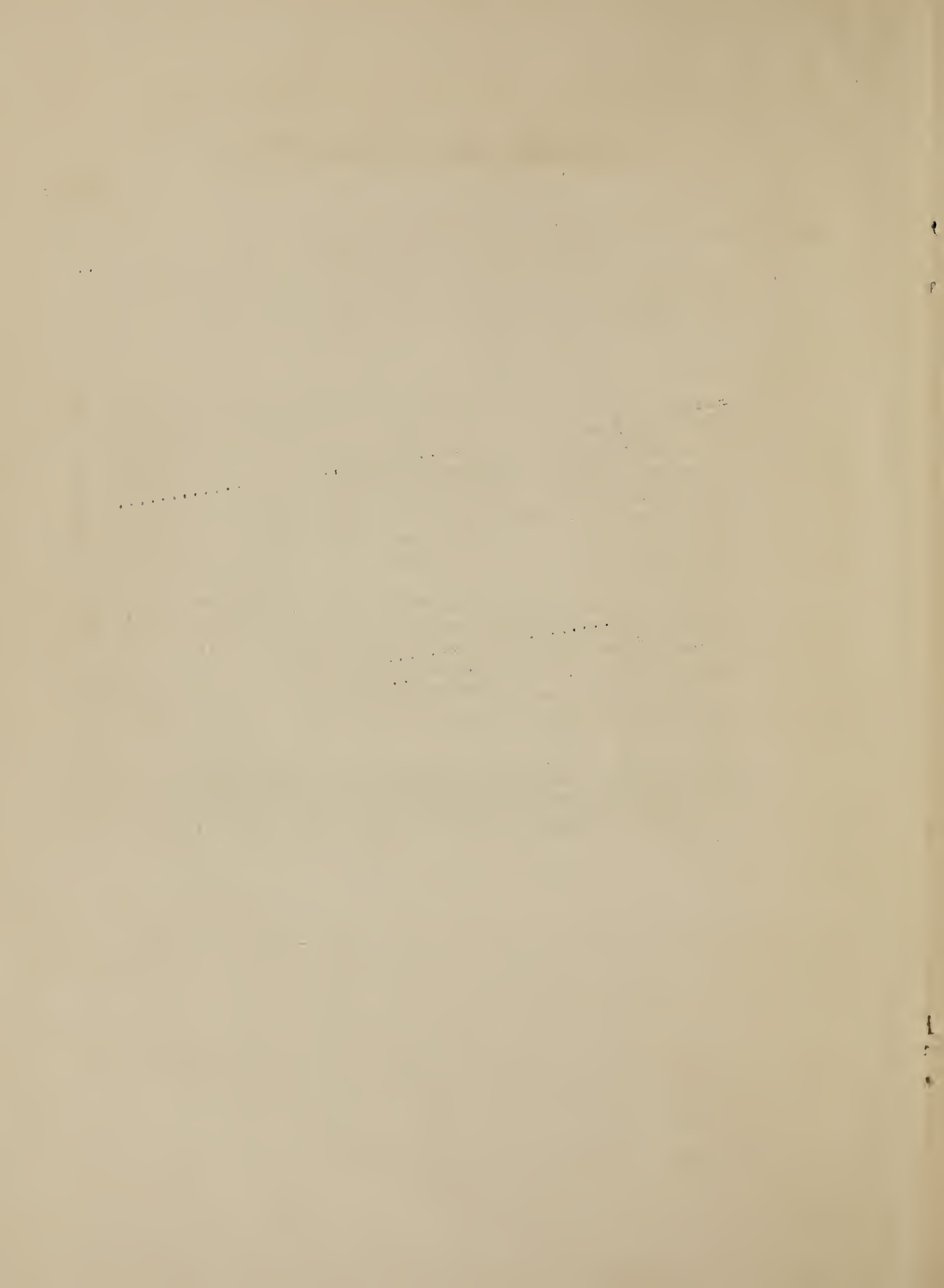
Revised, September 1939



**UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE
FOREST PRODUCTS LABORATORY
Madison, Wisconsin
In Cooperation with the University of Wisconsin**

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METHODS USED AT THE FOREST PRODUCTS LABORATORY FOR THE
CHEMICAL ANALYSIS OF PULPS AND PULPWOODS

Compiled by
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Revised September 1939¹

The following methods of analysis of woods and pulps have been compiled from various sources for the purpose of standardizing, as far as possible, the chemical evaluation of these materials. This compilation is primarily for the use of the Division of Pulp and Paper of the Forest Products Laboratory. It may, however, be of value to others confronted with the same problems. Wherever possible methods standard in the industry have been used, but many of the methods have been modified in the interest either of speed or of accuracy, as experience with them has dictated.

A knowledge of the chemical character of pulpwoods and of the chemical changes that the raw material undergoes during the various pulping reactions, or as a result of varying the conditions of treatment, affords a better understanding of the digestion, the bleaching, and the other reactions in pulp preparation. In addition it permits a more intelligent control in the subsequent processing of these materials to industrial products.

Application of certain of these analytical tests to pulps often enables one to detect deterioration of the materials used in their manufacture, or deterioration caused by over-cooking, so-called "burning," or subsequent treatments such as bleaching. In addition it is possible to determine the extent of decay in pulps during storage.

A better knowledge of the chemical nature of the various plant fibers used in the making of a given product may uncover properties that will permit substitution of less expensive raw materials, such for example, as the replacement of the long-fibered cotton cellulose, now common in many cellulose-using industries, by the less expensive wood pulp

In using these methods for the chemical examination of wood and wood pulps, it should be borne in mind that they have certain limitations in that complete wood analysis alone cannot give the specific information

¹Bray, M. W. Paper Trade J. 87 (25), 59 (December 20, 1928).

necessary for the establishment of the physical utilization of any wood. However, from certain specific determinations, together with the data obtained from practical pulping tests, relationships may be derived that may be used statistically in the interpretation of pulping and biological phenomena. Such information enables the investigator to solve his particular problem more satisfactorily.

PREPARATION OF MATERIALS

Sampling

The sample chosen for chemical analysis must be representative of the material under consideration.

Wood Sample

The wood sample is reduced to particles that will pass a 60-mesh standard sieve either (1) by cutting into sawdust with a circular saw according to the method described by Schorger² and then grinding in a disk mill of the Bauer type, or (2) by passing small pieces of the size of pulpwood chips through a Wiley laboratory type mill or a Koerner³ type mill.

A power sifter should be used in order to secure a better separation of the finely divided material, which clings tenaciously to the coarser particles, than can be done by shaking the sieves by hand. The portion remaining on an 80-mesh sieve is retained for analysis, while the portion passing the 80-mesh sieve is rejected. The air-dry sample is kept in a sealed glass jar, so that the moisture content is maintained approximately constant during the course of the analysis.

Pulp Sample

Pulps are air dried and then shredded to a fine fluffy condition either by means of a Koerner type mill or a "hammer and squirrel cage" shredder. The shredded material is also stored in sealed glass jars. At least 60 grams of material are required for a complete analysis.

If the sample of pulp represents raw or partially cooked material in softened chip form, it should be ground either in the disk mill or in the Koerner type mill and treated in the same manner as described for wood.

²Schorger, A. W. Ind. Eng. Chem. 9, 556 (1917).

³Bureau of Standards J. of Research, R. P. 295 (April 1934). Includes an illustrated description of the Koerner type of grinder.

ANALYTICAL PROCEDURE

All results except percentage of moisture are calculated and reported on the basis of the weight of the oven-dry material. The metric system is used throughout these methods, namely, all weights are in grams and volumes in milliliters.

Moisture

Gravimetric (See Note A)

Two to four grams of air-dry material are weighed in a glass-stoppered weighing bottle and are dried to constant weight in an oven at 105° C., which usually requires from 3 to 5 hours. The weighing bottle, containing the sample, is then closed, cooled in a desiccator over concentrated sulfuric acid, and weighed. Dry pulp is very hygroscopic and should therefore always be cooled and weighed in a closed vessel.

The percentage of moisture in the material is calculated by means of the following formula:

$$\frac{\text{Weight of moist sample} - \text{Weight of oven-dry material}}{\text{Weight of moist sample}} \times 100 = \text{Percentage of moisture in the material}$$

Volumetric

When essential oils or other volatile substances are present the moisture or water content of the material may be determined either according to the xylene method developed by Schwalbe⁴ or the toluene method⁵ of the Technical Association of the Pulp and Paper Industry.

According to the xylene method, approximately 25 grams of the sawdust are placed in a 500 ml. distilling flask and covered with water-saturated xylene. The water and xylene distill over together and the distillate, cooled by passing through a water condenser, is collected in a graduated tube provided with a funnel.

The distillate separates into two layers, the lower of which consists of water. The amount of water may be read off directly, since the essential oil is soluble in the xylene.⁶ The results are reported in percentage of

⁴Schwalbe, C. G. Z. Angew. Chem. 21, 408 (1908).

⁵Methods T-3 and 208-m, Official Standards (March 15, 1934) includes an illustrated description of the apparatus.

⁶Forest Service Circular 134.

water by weight, assuming each ml. of water to weigh 1 gram. The calculation is made according to the following equation:

$$\frac{\text{Volume or weight of water}}{\text{Weight of moist sample}} \times 100 = \text{Percentage of moisture in the material}$$

Should the subsequent analyses be made on air-dry material, the results may be calculated and reported on the oven-dry basis.

Note:

A.--Reference is made to Method No. T-210-m of the Technical Association of the Pulp and Paper Industry for methods of sampling commercial lots of pulps.

Ash^{1,2,7,8}

Three grams of oven-dry wood or pulp are incinerated in a shallow, tared, platinum dish in an electric muffle at a dull red heat. The contents of the dish are stirred occasionally, if necessary, with a stiff platinum or nichrome wire to insure complete combustion of the carbon.

If the combustion is incomplete the carbon will appear as a black suspended material on treatment with dilute hydrochloric acid. The ash is cooled in a desiccator over concentrated sulfuric acid and is weighed. The amount of ash is reported as a percentage of the oven-dry material. The percentage of ash in the sample is calculated as follows:

$$\frac{\text{Weight of ash}}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of ash}$$

Water Solubility

Cold Water^{1,9,10,11}

Two grams of air-dry material, the moisture content of which has been previously determined, or of oven-dry sawdust or pulp are placed in a

¹Schwalbe and Sieber. Betriels-Kontrolle in der Zells.und Papier Industrie.

⁸Methods T-211-m (September 15, 1936) and T-413-m (January 1938) of the T.A.P.P.I. Standard Methods.

⁹Schorger, A.W. "Chem. of Cellulose and Wood," 506 (1926). McGraw-Hill, N.Y.C.

¹⁰Hawley and Wise. "Chem. of Wood," 134 (1926), Chem. Catalogue Co., N.Y.C.

¹¹Methods T-1-m and T-207-m (March 15, 1934) of the T.A.P.P.I. Standard Methods.

400-ml. beaker and covered with 300 ml. of distilled water. This mixture is allowed to digest at room temperature with frequent stirring, for 48 hours. The material is transferred to a tared alundum crucible, is washed with cold distilled water, and is dried to constant weight at 105° C. in an air oven. Drying usually requires approximately 4 hours. The crucible is placed in a stoppered weighing bottle, is cooled in a desiccator over concentrated sulfuric acid, and is weighed. From the loss in weight caused by extraction, the percentage of material soluble in cold water may be calculated as follows:

$$\frac{\text{Oven-dry weight of sample} - \text{Oven-dry weight of extracted material}}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of cold water soluble material.}$$

The results are reported as a percentage of the oven-dry weight of the material.

Hot Water^{9, 10, 11}

Two grams of air-dry material, the moisture content of which has been previously determined, or of oven-dry sawdust or pulp, are digested with 100 ml. of distilled water in a 200 ml. Erlenmeyer flask provided with a reflux condenser. The flask is placed in a boiling water-bath, the water level of which is maintained constant, just above the solution in the Erlenmeyer flask, by means of a constant-level apparatus. (See Note B.)

After the water in the bath has boiled gently for 3 hours, the contents of the Erlenmeyer flask are transferred to a tared alundum crucible, washed with hot water, dried, cooled over concentrated sulfuric acid, and weighed in a stoppered weighing bottle. The amount soluble in hot water is calculated as a percentage of the oven-dry weight of material as follows:

$$\frac{\text{Oven-dry weight of sample} - \text{Oven-dry weight of extracted material}}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of material soluble in hot water.}$$

One Percent Caustic Soda Solubility^{1, 9, 10, 12}

Two grams of air-dry material, the moisture content of which has been previously determined, or of oven-dry wood or pulp are placed in a 250-ml. beaker to which is added 100 ml. of 1 percent sodium hydroxide solution (see Note C). The beaker is covered with a watch glass and is placed in a bath of boiling distilled water for exactly 1 hour. The height of the water in the bath is maintained level with the solution in the beaker by means of a constant-level flask. The contents of the beaker are occasionally stirred with a glass rod. The insoluble material is then collected in a tared alundum crucible, thoroughly washed successively with hot distilled water, dilute acetic acid (approximately 10 percent by weight), and hot

¹²Methods T-4-m and T-212-m (March 27, 1936). Official Standard Methods of the Technical Association of the Pulp and Paper Industry.

water, dried to constant weight in an air oven at 105° C., cooled in a stoppered weighing bottle placed in a desiccator over concentrated sulfuric acid, and weighed. The difference in the weight of the oven-dry sample and that of the oven-dry insoluble material is the portion soluble in alkali.

The percentage of material soluble in 1 percent sodium hydroxide solution is calculated as follows:

$$\frac{\text{Oven-dry weight of sample} - \text{Oven-dry weight of insoluble material}}{\text{Oven-dry weight of sample}} \times 100 =$$

Percentage of 1 percent NaOH soluble material.

The results are reported as a percentage of the oven-dry weight of the material.

The value for the alkali-solubility may be corrected for water solubility by subtracting the percentage of hot water soluble material from that of the 1 percent alkali soluble material. This correction is made under the assumption that all the material soluble in hot water is also soluble in 1 percent sodium hydroxide solution.

Note:

B.--The constant-level apparatus consists of a 3 to 5 liter balloon flask inverted above the water bath. Connection is made between the balloon flask and the water bath by means of glass tubing.

C.--The strength of the sodium hydroxide in the solution is determined by titration with standard acid using phenolphthalein and methyl orange, successively, as indicators.

10 Percent Potassium Hydroxide Solubility^{1,13}

Two grams of air-dry pulp or sawdust, the moisture content of which has been previously determined, or of oven-dry material are placed in a 250-ml. Erlenmeyer flask provided with a reflux air condenser with 100 ml. of 10.0 (± 0.1) percent caustic potash solution. The flask and contents are heated for 3 hours in a salt-water (NaCl) bath maintained at 100° C. An equivalent strength of sodium hydroxide solution, namely 7.14 (± 0.1) percent, may be substituted for the 10.0 percent potassium hydroxide solution.

Care must be taken to avoid concentration of the sodium hydroxide solution or undue oxidation of the pulp, caused by the exposure of the alkali-soaked material to the air. After the heating is completed the

¹³Pamphlet No. 450, Ordnance Dept., U.S.A. 16 (1918). See also U.S. Army Specification No. 50-11-44 for Cellulose (Sept. 29, 1930).

material and the solution are poured into a beaker containing 1 liter of distilled water, and the alkali is neutralized with a decided excess of glacial acetic acid, which causes the precipitation of some of the beta-cellulose. The undissolved material, together with the precipitated beta-cellulose are then filtered out using a weighed alundum crucible, and are thoroughly washed successively with hot water, alcohol, and ether. The washed material is then dried to constant weight at 105° C., which usually requires about 3-1/2 hours, cooled in a desiccator over concentrated sulfuric acid, and is weighed in a stoppered weighing bottle. The loss in weight is then calculated as the percent "KOH soluble" content, using the same formula as reported for the determination of 1 percent alkali solubility. The results are reported as a percentage of the weight of the oven-dry material and may be calculated according to the equation for the 1 percent caustic soda solubility.

Ether Solubility^{1,2,9,10,14}

Two grams of the air-dry material, the moisture content of which has been previously determined on a separate sample, are weighed in a tared alundum crucible (porosity R.A. 98) contained in a glass-stoppered weighing bottle. The crucible is removed from the bottle and placed in a Soxhlet apparatus. A small cone of fine mesh screen wire is set in the top of the crucible to prevent loss of sample by spattering. The sample is extracted for 6 to 8 hours with approximately 200 ml. of U.S.P. ethyl ether, keeping the ether boiling briskly. The amount of material extracted may be determined either by weighing the extracted residue after evaporation of the solvent, or by determining the loss in weight of material resulting from extraction. According to the first procedure, the ether is evaporated from the extraction flask, which is dried in an oven for 1 hour at 105° C., cooled in a desiccator and weighed. The drying is continued until there is no further loss in weight. The weight of the dried residue is calculated to the percentage of the oven-dry material and reported as the percentage of ether-soluble matter.

According to the second procedure, the extracted material and alundum crucible are dried to constant weight in an air oven at 105° C., replaced in the glass-stoppered weighing bottle, cooled in a desiccator over concentrated sulfuric acid, and weighed. The results of the two procedures seldom agree and the former is recommended as the more accurate method. The disagreement in the results of the two procedures is due to one or more of four things, (1) some of the extracted substances volatilize during drying⁹; (2) some of the solvent remains included within the extract and is not entirely removed during the evaporation procedure¹⁰; (3) loss of sample as a result of spattering; (4) oxidation of the extracted material during drying. Though the extracted pulp residue may be used for the determination of lignin, wood residues should first be extracted with alcohol-benzene mixture previous to the determination of lignin.

¹⁴Methods T-5-m (August 15, 1936) Official Standard Methods T.A.P.P.I.

Alcohol-Benzene Solubility^{1,15}

In addition to the substances removed by ethyl ether, possibly some of the so-called wood gums are dissolved by extraction with a mixture of 33 percent alcohol and 67 percent benzene (by volume).

Approximately 2 grams of air-dry wood, sawdust, or pulp, the moisture content of which has been previously determined, are weighed in a tared alundum crucible contained in a weighing bottle.

The crucible with its contents is extracted 4 to 8 hours in a Soxhlet extractor with the alcohol-benzene mixture described in the preceding paragraph. After evaporation of the solvent the sample is dried to constant weight at 105° C. The percentage of extracted material may be determined either from the loss in weight of the sample or from the weight of the extract after evaporation of the solvent in the drying oven.

The percentage of material soluble in alcohol-benzene mixture is calculated as follows:

$$\frac{\text{Oven-dry weight of alcohol-benzene extract}}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of alcohol-}$$

benzene soluble material.

If the extracted residue is to be used for the subsequent determination of cellulose or lignin, the crucible and contents are removed from the Soxhlet apparatus, dried at 105° C. to constant weight, replaced in the weighing bottle, cooled in a desiccator, and weighed. The results are reported as the percentage of alcohol-benzene soluble matter (oven-dry basis).

Lignin

The lignin¹⁶ or noncarbohydrate content of the extractive-free wood substance or pulp is determined by certain modifications of the method of Ost and Wilkening¹⁷ employed for the hydrolysis of cellulose. Although several modifications of the method^{18,19,20,21} including the control of

¹⁵Method T-6-m (August 15, 1936) Official Standard T.A.P.P.I.

¹⁶Klason, P. Paper Industry 4, 262 (May 1922).

¹⁷Cross and Bevan. "Researches on Cellulose, III," 39 (1905-10); Chemiker Zeit. 34, 461 (1910).

¹⁸Norman and Jenkins. Biochem. J. 28, 2147 (1934).

¹⁹Peterson and Walde. Ind. Eng. Chem., Anal. Ed., 4, 216 (1932).

²⁰Ross and Hill. Pulp and Paper Mag. Can. 27 (15), 541 (1929).

²¹Schwalbe, H. Papier-Fabr. 23, 174 (1925).

time,²² temperature,^{22,23} and the use of various pretreatments for the removal of the extractives,^{22,24,25,26,27} such as fats; waxes, tannins, and the like, have been proposed to take care of certain peculiarities of species; essentially, the method consists of the solution and subsequent hydrolysis of the cellulosic compounds with 72 and 3 percent sulfuric acid solutions, respectively. Some judgment as to the necessity of using the different pretreatments^{28,29,30} must be exercised. For example, pulps of a relatively high degree of purity require no preliminary extraction with organic solvents, and woods free of tannins do not require an extraction with 95 percent ethyl alcohol. However, in analyzing woods in which the nature of the extractives is not known, such an extraction is a safeguard.²⁴ The control of time and temperature of treatment with 72 percent sulfuric acid is essential in order to prevent the decomposition of cellulosic compounds which would appear in the lignin residue.

Procedure

Approximately 2 grams of air-dry wood in the form of sawdust (60 to 80 mesh) or shredded pulp, the moisture content of which has been previously determined, are weighed into a tared alundum crucible. The material is extracted for 4 hours in a Soxhlet apparatus with 95 percent ethyl alcohol. (This extraction may be omitted in the case of pulps and tannin-free woods.) The material is next extracted for 4 hours with alcohol-benzene solution (1 to 2 parts, respectively, by volume). The solvent is removed by suction, the residue washed with alcohol by suction to remove the benzene and then extracted for 3 hours with 400 ml. of hot water in a hot-water bath, filtered, washed with hot water, and finally dried. Because of the small amounts of extractives in pulps, the extraction operation may usually be dispensed with and the samples may be weighed and dried in weighing bottles directly. The dried material is transferred from the crucibles to weighing bottles, divided into fine particles, and triturated with 40 ml. of 72.0 (+0.1)^{22,31,32} sulfuric acid (by weight) at 20° C. The acid should be

²²Ritter, Seborg, and Mitchell. Ind. Eng. Chem. 4, 202 (1932).

²³Sherrard and Harris. Ind. Eng. Chem. 24, 103 (1932).

²⁴Ritter and Barbour. Ind. Eng. Chem., Anal. Ed. 7, (4), 238 (1935).

²⁵Cohen and Dadswell. "Chemistry of Wood, Pt. 1." Melbourne, Commonwealth of Australia, Council of Scientific and Industrial Research, 1931.

²⁶Mahood and Cable. Ind. Eng. Chem. 14, 933 (1922).

²⁷Harris, E. E. Ind. Eng. Chem., Anal. Ed. 5, 105 (1933).

²⁸Campbell and Bamford. J. Biochem. 30, 419 (1936).

²⁹Cohen and Harris. Ind. Eng. Chem., Anal. Ed. 9, 234 (1937).

³⁰Harris and Mitchell. Ind. Eng. Chem. Anal. Ed. 11, 153 (1939).

³¹Becker, E. Papier-Fabr. 17, 1325 (1919).

³²Klason, P. Svensk. Pap. Tid. 19, 129 (1916).

added in small portions and mixed thoroughly with the material, care being taken not to allow the temperature to exceed 20° C. during the entire reaction period of 2 hours. The resulting mixture is transferred to a 2-liter Erlenmeyer flask, diluted with 1,503 ml. of distilled water, making the concentration of sulfuric acid exactly 3 percent, and boiled for 3 hours under a reflux condenser. The residue is filtered on a tared alundum crucible, washed free of acid by means of hot water, dried to constant weight at 105° C. in an oven, cooled in a glass-stoppered bottle in a desiccator, and weighed. The lignin content of the material is calculated as a percentage of the oven-dry unextracted wood or pulp.

In case a correction for ash is desired, the lignin is transferred to a tared platinum dish and the ash content determined in the usual manner.

Holocellulose

Holocellulose,³³ a white lignin-free solid is composed of the cellulose and the hemicellulose fractions of wood. Essentially, the method³⁴ for the estimation of this material consists of the removal of lignin only from extractive-free wood (extracted successively with 95 percent ethyl alcohol, with alcohol-benzene mixture, and with hot distilled water as previously described in the determination of lignin) by means of a chlorination and a suitable lignin chloride solvent (95 percent ethyl alcohol containing 3 percent by weight of monoethanolamine) without destruction of either the so-called "Cross and Bevan" cellulose or the hemicelluloses.

Procedure

Approximately 2 grams of air-dry wood, the moisture content of which has been previously determined, are weighed into a tared alundum crucible, extracted for 4 hours in a Soxhlet apparatus with 95 percent ethyl alcohol and then for a like period with alcohol-benzene (1 to 2 by volume) mixture. The residue is washed with alcohol to remove the benzene and extracted with 400 ml. of hot distilled water in an Erlenmeyer flask for 3 hours in a boiling-water bath. The residue is filtered on a 35-ml., No. 3 Jena fritted-glass (porosity 5 to 7) bottom crucible, washed first with hot distilled water and finally with cold (10° C.) distilled water, removing the excess moisture by suction. Suction is applied first at the bottom of the crucible until the excess moisture is removed, and then at the top. The suction at the top removes the water from the fritted glass plate and distributes the remaining moisture evenly throughout the entire sample. The crucible is connected to a source of chlorine gas and the material is chlorinated as described in the method for the determination of cellulose by passing chlorine gas up through the bottom of the fritted-glass crucible. After 3 to 5 minutes' chlorination, the crucible is removed from

³³Ritter and Kurth. Ind. Eng. Chem. 25, 1250 (1933).

³⁴Van Beckum and Ritter. Paper Trade J. 105 (18), 127 (October 28, 1937).

the apparatus and ethyl alcohol is added to dissolve the excess chlorine and hydrogen chloride. After 1 minute of contact the alcohol is removed by suction, the vacuum is released, and sufficient hot (minimum temperature 75° C.) alcohol-monoethanolamine (95 percent alcohol containing 3 percent of monoethanolamine) is added to cover the wood completely. The material is thoroughly stirred and allowed to stand for 2 minutes, when the lignin solvent is removed by suction. The material is again treated with the hot solvent as before, washed first with 95 percent ethyl alcohol to remove any solvent remaining, and then twice with cold water. After removing excess water by suction applied first at the bottom then at the top of the crucible as previously described, the chlorination and extraction treatments are repeated until the residue becomes white following chlorination and is no longer colored by the addition of the hot lignin chloride solvent. At this point the material is transferred to a tared alundum crucible and the alcohol-monoethanolamine is finally removed by washing twice with alcohol, twice with cold water, and again with alcohol until the residue is neutral to litmus, and finally with ethyl ether to facilitate drying. The holocellulose is first air dried to remove ether so as to guard against explosions, and then dried to constant weight in an air oven at 105° C.

The holocellulose is calculated as a percentage of the unextracted wood.

Cellulose

Cross and Bevan³⁵ in 1880 announced that lignocelluloses when treated with dilute sodium hydroxide solution and then with chlorine gas and dilute sodium sulphite solution yielded a white product resembling cotton cellulose. This procedure is the basis of the most reliable method for the determination of cellulose at the present time.

It has been shown² that higher yields of cellulose were obtained by omitting the initial treatment of the wood with 1 percent sodium hydroxide solution.

In the original methods^{2, 35} the chlorination treatments were long, ranging from 30 minutes for the first chlorination to 15 minutes for the last. Prolonged action of chlorine gas³⁶ together with the hydrochloric acid formed hydrolyses the cellulose, causing the alpha-cellulose content to vary.

Ritter³⁷ has shown that the chlorination periods may be shortened to 3 minutes for the first chlorination and that even in this short period the same quantities of lignin and substances other than cellulose are

³⁵Cross and Bevan. J. Chem. Soc. 38, 666A (1880); Chem. News 42, 77-91 (1880); J. Chem. Soc. 55, 199 (1889).

³⁶Bray and Andrews. Paper Trade J. 76 (8), 47 (February 22, 1923).

³⁷Ritter, G. J. Ind. Eng. Chem. 16, 947 (1924).

removed. The cellulose thus isolated is in as pure form as when treated with chlorine gas for the longer periods.

Dore³⁸ devised a special apparatus for chlorinating the material directly in a crucible, and Roe³⁹ described a method for determining the percentage of chlorine absorbed by unbleached sulphite pulps.

By the application of the principles of the last two methods to the modified methods of Schorger and of Ritter for cellulose estimation in wood and wood pulps, it is possible to determine in addition to cellulose the amount of chlorine required for the isolation of the cellulose. The data thus obtained in the case of pulps furnish an indication of the relative bleach requirements.

Procedure⁴⁰

Approximately 2 grams of air-dry wood (60 to 80 mesh) or pulp, the moisture content of which has been previously determined, are weighed into a tared alundum crucible held in a glass-stoppered weighing bottle. The crucible and contents, in the case of wood, are placed in a Soxhlet apparatus and extracted for 6 hours with alcohol-benzene mixture (1 to 2 by volume, respectively), dried by suction, washed with alcohol to remove benzene, and finally with water to remove the alcohol. The extraction may usually be dispensed with in the case of pulps. The moist material is transferred to a 35 ml., No. 3, fritted, glass-bottom Jena glass crucible (Note D). Suction (Note E) is applied first at the bottom of the crucible until excess moisture is removed and then at the top, which removes the water from the fritted glass plate and distributes the remaining moisture evenly throughout the entire sample. The crucible is then connected to a supply of chlorine gas and the material is chlorinated (Note D) for 3 to 4 minutes as described below. Where the amount of chlorine required to isolate the cellulose is desired the entire apparatus shown in Figure 1 should be employed, according to the following directions; otherwise, the gas burette and Hempel gas pipette may be omitted. A measured quantity of chlorine gas is forced from the burette up through the material in the crucible and over into the Hempel gas pipette as rapidly as possible. During the first chlorination, samples of wood absorb approximately 230 ml. of chlorine gas at room temperature and atmospheric pressure; this necessitates refilling the burette, which may be done quickly, since it is connected to a chlorine tank with a three-way stopcock. After chlorinating the material for from 3 to 4 minutes, the crucible is removed from the apparatus and the material is washed with cold, distilled water, using suction. These washings are saved for subsequent determination of the hydrochloric acid formed. The material is next washed successively with 50 ml. each of a 3 percent sulfurous acid solution, cold water, and a freshly prepared 2 percent sodium sulfite solution. The

³⁸Dore, W. H. Ind. Eng. Chem. 12, 264 (1920).

³⁹Roe, R. B. Ind. Eng. Chem. 16, 808 (1924).

⁴⁰Bray, M. W. Ind. Eng. Chem. Anal. Ed. 1 (1), 40 (January 15, 1929).

material is transferred to a 250-ml. Pyrex beaker with the aid of a pointed glass rod, and treated with 100 ml. of a 2 percent solution of sodium sulfite. The last traces of the sample adhering to the porous bottom of the crucible are removed by successively drawing 10 ml. portions of the sodium sulfite solution up through the bottom of the crucible by means of suction. (Note E.) A rubber policeman drawn gently over the bottom of the crucible assists materially in loosening particles of the material adhering to the fritted glass plate. The beaker containing the material is covered with a watch glass and held in a boiling water bath for 30 minutes with occasional stirring, the contents are then filtered, washed with 250 ml. of hot distilled water, and again chlorinated as before. This operation is repeated until the chlorinated material is a uniform white or shows only a faint tinge of pink upon addition of the sodium sulfite solution. Coniferous woods require as many as four or more chlorinations; hard-woods usually require less.

After the final digestion with sodium sulfite solution the cellulose fibers are filtered, washed with hot water, and digested for 2 hours on a water bath in a beaker with 200 ml. of distilled water (Note F). The cellulose (Note G) is filtered on a tared alundum crucible, washed successively with 500 ml. of hot distilled water, 50 ml. of 95 percent alcohol, and finally with 50 ml. of ethyl ether (Note H). The ether is removed by suction and the material is first air dried to avoid explosions and then dried at 105° C. to constant weight in an air oven which usually requires 2-1/2 to 3 hours. The crucible, placed in a stoppered weighing bottle, is cooled in a desiccator over concentrated sulfuric acid and weighed.

The cellulose is calculated as a percentage of the oven-dry unextracted wood or pulp as follows:

$$\frac{\text{Oven-dry weight of cellulose}}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of cellulose.}$$

Note:

D.--If a fritted glass bottom crucible is not available, the material may be chlorinated directly in the alundum crucible according to the method of Dore,³⁸ or it may be transferred to a 250-ml. beaker and treated with chlorine gas in the apparatus described by Schorger,² in which cases a clean alundum crucible should be used for finally collecting and weighing the cellulose as the one used throughout the several treatments contains salts, which are difficult to remove.

E.--A large perforated rubber stopper connected to a suction pump may be pressed against the top or bottom of the glass crucible for the purpose.

F.--The digestion of cellulose with water and thorough washing with hot water is necessary to remove traces of acids which are persistently retained. If the cellulose is incompletely washed, as may happen if washing is performed in the crucible, it may darken during drying. Furthermore, the removal of salts and acids by means of the digestion in hot water will

eliminate hydrolysis of the cellulose residue during drying in the oven. This is especially important if the alpha-cellulose determination is to be made on the Cross and Bevan cellulose as the hydrolysis during drying produces considerable quantities of water-soluble material.

G.--To obtain a snow-white product the cellulose may be bleached by adding 20 ml. of 0.10 percent potassium permanganate solution to the cellulose (after the final digestion with sodium sulfite and washing out of sodium sulfite); allow to stand 10 minutes and render colorless with sulfur dioxide water. It is then filtered, washed, returned to the beaker, 200 ml. of water added, and heated on the steam bath with occasional stirring for 2 hours. The remaining procedure for washing and drying is the same as above. The bleaching may be omitted, since the yields of unbleached and bleached cellulose agree within a few tenths of 1 percent.

H.--The alcohol and ether used in washing should be free of acids. Washing with alcohol and ether prevents the cellulose from drying to a hard mass as the water is removed.

Chlorine Consumption in the Isolation of Cellulose⁴⁰

This value, obtainable during the isolation of cellulose, is a measure of the total amount of chlorine gas actually consumed by compounds other than cellulose in wood or pulp. Such values for a series of pulps are indicative of their relative bleachabilities and with a sufficient background of data may be used to predict actual bleach requirements.

Procedure

The procedure previously described for the isolation of cellulose, together with certain additional steps is employed.

A measured quantity of chlorine gas (approximately 90 ml.), noting the exact amount, is run into the gas burette shown in Figure 1. The gas is passed up through the material contained in a water-jacketed 35-ml., No. 3, fritted glass bottom crucible (porosity 5 to 7) and over into a Hempel gas pipette (Note I). The unconsumed gas is returned to the burette and the exact amount measured. The total volume of gas consumed is obtained by difference. The Jena glass crucible containing the material is connected to a clean suction filter flask and the material is washed with four 25-ml. portions of water at a temperature of approximately 20° C. The filtrate is labeled and kept in a stoppered flask.

At each successive chlorination the above procedure is repeated and the total volume of chlorine consumed is corrected to standard conditions of temperature and pressure, namely, 0° C. and 760 mm., taking into consideration the vapor pressure of water vapor at the chlorination temperature over a saturated CaCl_2 solution saturated with chlorine gas. The calcula-

tion is made according to the following formula:

$$V_o = \frac{V_1 \times (p - a)}{760(1 + 0.00367t)}$$

where V_1 = volume of gas observed at t degrees C.

V_o = volume of gas under standard conditions

a = vapor pressure of water vapor over saturated CaCl_2 solution saturated with chlorine gas in mm. of mercury at t degrees C.

t = temperature of chlorination in degrees C.

p = observed barometric pressure in mm of mercury.

The following table is of assistance in making these calculations:

$t^\circ\text{C.}$	a	$760 \times (1 + 0.00367t)$
23.5	15.9	826.00
24.0	16.6	826.90
24.5	17.3	828.36
25.0	18.0	829.76
26.0	19.4	832.57
27.0	20.8	835.40
28.0	22.0	838.12
29.0	23.5	840.96
30.0	25.0	843.66
31.0	26.4	846.48
32.0	29.0	849.30

The weight of 1 ml. of chlorine gas at standard temperature and pressure = 0.003164 gm. The percentage of chlorine consumed may be obtained by substitution of the proper values in the following formula:

$$\frac{V_o \times 0.003164}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of chlorine consumed.}$$

The percentage of chlorine forming hydrochloric acid during chlorination is determined by titrating the combined initial wash waters with standard alkali.

Note:

I.--A 2-gram sample of wood will absorb approximately 230 ml. of chlorine gas at 20° C. under atmospheric pressure. Hence, refilling of the burette several times is necessary.

Chlorine Number of Pulp

The chlorine number of pulp is the weight in grams of gaseous chlorine that is absorbed in 15 minutes in a single operation at 20° C. by 100 grams of oven-dry pulp, the moisture content of which is 55 percent during the test. The method, originally devised by Roe³⁹ and modified by several investigators,⁴¹ is essentially that described by Johansson.⁴²

Apparatus

The apparatus, as illustrated in Figure 2, consists of a 200 ml. aspirator bottle A, a water-jacketed 100 ml. gas measuring burette B, a specially-made reaction bottle C of 50 ml. capacity, capable of holding 2 grams of shredded pulp, and a 200-ml. U-tube D, all connected with capillary tubing and stopcocks. The outside dimensions of reaction bottle C are 2-1/2 inches in height to the bottom of the neck and 1-1/2 inches in diameter. A number 25 standard ground glass joint is employed. During the determination the reaction bottle is maintained at 20° C. by immersion in a 250 ml. beaker filled with water. The bottle is held in place with a rubber sponge placed in the bottom of the beaker. The U-tube D is made of 11/16-inch, outside diameter, glass tubing, each leg being 24 inches in length. A solution of calcium chloride containing 30 grams per 100 grams of water, saturated each day with chlorine gas, is used in the apparatus.

The steaming apparatus consisting of a steam generator is made of a 1-liter Florence flask connected to the reaction bottle with a delivery tube and a water trap. The end of the delivery tube should reach just to the bottom of the neck of the reaction bottle, which is placed on the pan of a triple-beam type balance. The steam generator is heated with a Bunsen burner.

⁴¹Genberg and Jonsson. Paper Trade J. 82 (22), 50 (June 3, 1926).
Genberg and Houghton. Paper Trade J. 88 (17), 71 (April 25, 1929).
Yorston, F. H. Forest Prod. Lab. of Can. Research Notes, Vol. II, 21 (1929).
⁴²Johansson, David. Paper Trade J. 101 (13), 101 (September 26, 1935).

Procedure

Approximately 2 grams of air-dry pulp are weighed in a tared glass-stoppered weighing bottle, dried for 2-1/2 hours at 105° C., cooled in a desiccator, and weighed. The dry pulp is transferred to reaction bottle C (Fig. 2) and by means of a pointed rod a hole is made vertically through the pulp at the center of the bottle sufficiently large to receive the delivery tube of the steaming apparatus and the gas delivery tube of the chlorination apparatus.

The reaction bottle is placed on the pan of a triple beam balance and connected through a trap with the steaming apparatus (Note J). Steam is admitted to the pulp until the bottle and its contents has increased 2.5 grams in weight, when the reaction bottle is removed, closed with a rubber stopper, cooled to 20° C., and connected by means of the greased, ground-glass joint to the chlorination apparatus. During the chlorination the reaction bottle is held at 20° C. by means of a water jacket at the bottom of which is a rubber sponge for holding the reaction bottle in place.

Before chlorination of the pulp sample the calcium chloride solution, consisting of 30 grams of calcium chloride per 100 grams of water, in the apparatus (burette B, leveling bottle A, and U-tube D) is saturated with chlorine gas at least once a day. Using an empty reaction bottle C in place of the one containing the pulp sample, chlorine gas is lead into U-tube D through cock K₃. After saturation, the liquid in the U-tube is sucked to the top (constricted point X) of the left arm and cock K₃ is closed. The liquid in the burette B and leveling bottle A is next saturated with chlorine by passing the gas slowly through the water-jacketed burette and over into the solution which will be forced into the leveling bottle A. The chlorine in burette B is then released by opening cocks K₁ and K₂ to the atmosphere and raising bottle A. The burette is rinsed twice with chlorine gas and refilled. Bottle A is so placed by means of an adjustable clamp that the surface of the liquid is the same as that in the burette and after standing for 2 minutes with cock K₁ closed to allow the temperature of the gas to come to equilibrium with the water in the jacket of the burette, the volume of chlorine in burette is read. Turning cocks K₁, K₂, and K₃ so as to connect B, C, and D and raising bottle A, the gas is allowed to flow until the whole system is at atmospheric pressure, when A is again lowered until the surface of the liquid in the left arm of D again reaches the reference point X. K₃ is then closed, bottle A is leveled with the liquid in burette B, and the volume of gas in the burette is again read. If the apparatus is in proper working condition and free from leaks (Note K) the initial and final readings should not vary more than 0.2 or 0.3 ml.

The burette is emptied, refilled with fresh chlorine gas, cock K₁ is closed, and reaction bottle C containing the sample is connected, being pressed into place with the rubber sponge in the bottom of the water jacket, which contains enough water at 19° to 19.5° C. to extend as high

as the pulp in the reaction bottle. Cock K_2 , momentarily opened to the atmosphere to relieve any pressure in the reaction bottle, is turned to make connection with the burette. The volume of chlorine gas in the burette is read and recorded. Cock K_1 followed by cock K_3 is opened and chlorine gas is passed through the sample in reaction bottle C over into U-tube D by raising bottle A so that the surface of the liquid in A is level with that in the burette. The chlorine is allowed to react for exactly 15 minutes, bottle A being raised occasionally to the level of the liquid in the burette. In the case of very raw pulps requiring more than 50 ml. of chlorine, burette B is refilled with chlorine, after noting the volume of gas remaining in the burette.

The interruption in gas flow during the refilling operation is not long enough to cause any appreciable error as chlorine may be sucked back into the reaction bottle from U-tube D during the interruption. For very raw pulps, 50 ml. of additional chlorine are sufficient.

After the chlorine has reacted for 15 minutes, bottle A is lowered until the liquid in the left arm of U-tube D is drawn up to the reference point X when cock K_3 is closed. The liquid in bottle A is leveled with that in the burette and the volume is read. The difference between this and the total volume added is the volume of chlorine gas, at atmospheric pressure, and the temperature of the water jacket that has reacted with the pulp. Since the moisture in the pulp absorbs chlorine gas, a correction for the volume thus absorbed must be made by running a blank determination on a 2-gram sample of bleached pulp. Blank determinations have been found to have an average value of 4.0 ml. of chlorine gas.

In preparation for each succeeding determination the apparatus should be flushed with chlorine gas.

The chlorine number of pulp is calculated from the following equation:

$$\text{Chlorine number} = (V - 4) \times \frac{273}{T} \times \frac{h}{760} \times \frac{70.9}{22.414} \times \frac{100}{w}$$

where V is the volume in ml. of chlorine gas absorbed; h is the atmospheric pressure in mm. of mercury; w is the weight of the sample in grams; and T is the absolute temperature = $t + 273$.

All the constants in the above equation may be grouped into one factor, 0.1138, leaving the following simplified equation:

$$\text{Chlorine number} = \frac{0.1138 \times (V - 4) \times h}{w \times T}$$

Note:

J.---It has been found convenient when running a number of samples to

prepare and steam as many as there are extra reaction bottles, but leaving one in the chlorination apparatus.

K.--The chief difficulty in obtaining check results is due to imperfect seals in the stopcocks, particularly K_1 and K_2 . The stopcocks should be cleaned frequently, greased with vaseline, and finally with syrupy phosphoric acid.

Alpha-, Beta-, and Gamma-Cellulose

The determination of the alpha-, beta-, and gamma-cellulose⁴³ in cellulose isolated from wood by the chlorination method or directly in pulps (Note L) is a measure of the resistance of the cellulose or pulp to the action of Mercer's solution, 17.5 (+0.2) percent (by weight) sodium hydroxide solution. In cases where the alpha-cellulose content of a cellulose or a lignin-free (Note L) pulp alone is desired, or when the alpha-cellulose is not difficult to filter and wash, the gravimetric method is recommended. When data on all three constituents are desired, however, the work may be facilitated by using the volumetric method.⁴⁴

Gravimetric Method for the Determination of Alpha Cellulose⁴⁵

The method, while slightly modified to take care of small samples of material remaining from the cellulose determination, is essentially that adopted by the Division of Cellulose Chemistry of the American Chemical Society.⁴⁶

⁴³Cross and Bevan. "Researches on Cellulose" III, (1905-10) 23; "Paper Making" (1916), 97; Schwalbe, "Chemie der Cellulose," (1911), 637; Jentgen, Kunststoffe, 1, 165 (1911); Mag. Jahr., 57, 426 (1911); Z Angew. Chem. 24, 1341 (1911); Opfermann, "Die Chemische Untersuchung Pflanzliche Rohstoffe und der daraus abschiedenen Zellstoffe," translated by C. J. West, Paper 8, 19 (1921); Bronnert, "Die Chem. Unter. etc.," Berlin (1920); Schwalbe & Sieber, "Die Chemische Betriebs-Kontrolle in der Zellstoffe und Paper Industries," 151; Bray & Andrews, Ind. Eng. Chem. 15, 377, (1923); Cellulose Chemie 4, 115 (1923); Zellstoff und Papier, 3, 109 (1923); Paper Makers Mo. J., London, 61, 5 (1923); Sherrard & Blanco, Ind. Eng. Chem. 14, 64 (1922); D'ans and Jaeger, Cellulose Chemie 6, 137 (1925).

⁴⁴Bray and Andrews. Ind. Eng. Chem. 15, 377 (1923); Paper Trade J. 77, No. 8, 51 (August 23, 1923).
Cf. Launer, H. F. J. Research Natl. Bureau of Standards 20, 87 (Jan. 1938).

⁴⁵Schwalbe, C. G. Papier-Fabr. 23, 477, 697 (1925); ibid 26, 189 (1928).
Ross, Research Notes, Can. Pulp & Paper Assn. 1, 37, 57 (1926). Parsons, Paper Trade J. 82 (8), 211 (1926). Porrvik, Papier-Fabr. 26, 81, 120, 133, 151, 179 (1928). Jahn and Wise, Paper Ind. 10, 250 (1928).

⁴⁶Ritter. Ind. Eng. Chem., Anal. Ed., 1 (1), 52 (January 15, 1929).

Procedure

Approximately 1 gram of oven-dry cellulose, obtained from the previously described chlorination method, or of air-dry lignin-free pulp (Note L), the moisture content of which has been previously determined on separate duplicate samples, is accurately weighed in a weighing bottle and transferred to a 250-ml. Pyrex beaker. Twenty-five ml. of a 17.5 percent (by weight) carbonate-free sodium hydroxide solution (Note M) cooled to 20° C. are measured out in a small graduate. Ten ml. of this solution are added to the pulp in the beaker maintained at 20° C. in a water bath and allowed to stand for 5 minutes. With a short glass rod, the end of which has been flattened out to form a small disk, the material is macerated for 10 minutes, during which interval the remaining 15 ml. of sodium hydroxide solution (20° C.) are added intermittently in 5-ml. portions. The beaker is covered with a watch glass. After 30 minutes additional mercerizing treatment in the 20° C. water bath (total mercerization time, 45 minutes) 25 ml. of distilled water at 20° C. are added to the alkali-cellulose mixture followed by thorough stirring. The contents of the beaker are filtered immediately by means of suction either into a 30 ml. tared Jena 1bG3 fritted glass bottom crucible, a Gooch (Note N), or a tared alundum crucible (porosity R.A. 98). The residue in the crucible is washed first with 100 ml. of 8.3 percent sodium hydroxide solution (20° C.), and finally with 250 ml. of distilled water (20° C.) by means of suction. After releasing the suction, 15 ml. of 10 percent acetic acid (20° C.) are added and allowed to react for 5 minutes, when the suction is again applied to remove the acid. The alpha-cellulose is washed with distilled water (20° C.) until free from acid. Litmus paper is used to test the last portions of wash water passing through the crucible, and when free from acid an additional 250 ml. of distilled water (20° C.) are applied.

Excess water is removed from the outside and bottom of the crucible with a cloth and the crucible, together with the weighing bottle, is dried in an oven at 105° C. to constant weight -- that is, the first consecutive constant weights (0.0005 gram or less) obtained after 1-hour heating intervals following an initial drying period of at least 6 hours. Before the crucible is removed from the drying oven, it is placed in its weighing bottle, which is then closed. The covered weighing bottle and its contents are allowed to cool to room temperature in a desiccator over concentrated sulfuric acid before weighing.

The alpha-cellulose yield is calculated as a percentage of the oven-dry material tested according to the following equation:

$$\frac{\text{Oven-dry weight of alpha-cellulose}}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of alpha-cellulose.}$$

Results are reported to tenths of a percent.

Note:

L.--A small amount of lignin impurity, remaining in the pulp, is not separated from the alpha-cellulose in the gravimetric method and an error is introduced by its presence. Correction should, therefore, be made for such insoluble substances.

M.--Preparation of 17.5 percent sodium hydroxide solution. The sodium hydroxide solution is prepared by dissolving the sticks of caustic alkali in an equal volume of water and allowing the solution to stand for 10 days to precipitate the carbonate and other impurities. The clear supernatant liquid is decanted and diluted with carbon dioxide-free water until its density at 15° C. is 1.194 (± 0.001) or 1.192 at 20° C. (Int. Crit. Tables Vol. III, p. 79.) Such a solution contains 17.5 ± 0.1 grams of sodium hydroxide per 100 grams of solution.

N.--Filtering medium. If a Gooch crucible is used (one with a finely perforated bottom must be chosen) the cellulose is allowed to form its own mat, in which case it is necessary to pour the filtrate through the mat a second or third time to catch the fine particles.

Volumetric Methods for the Determination of Alpha-,
Beta-, and Gamma-Celluloses⁴⁴

Since, in the volumetric method, the alpha-cellulose after isolation is dissolved in 72 percent (by weight) sulfuric acid and is determined by titration, it is not necessary to wash it free from sodium hydroxide. Removal of the last traces of sodium hydroxide from the alpha-cellulose is very difficult when the original cellulose contains a high percentage of beta-cellulose, since this renders the alpha-cellulose difficult to wash. In some cases, especially when large amounts of beta-cellulose are present, it is impossible to separate the alkali-insoluble and alkali-soluble cellulose (alpha- and beta-cellulose) by filtration through a porous crucible as the cellulose mass becomes very jelly-like. In such cases, the alkali-treated cellulose is placed in tubes and centrifuged until the alpha-cellulose separates at the bottom of the tube. The supernatant liquid is decanted from the alpha-cellulose and the latter is successively washed by decantation and centrifuging first with 8.3 percent sodium hydroxide solution (50 ml.) and then with distilled water until the total washings amount to approximately 350 ml.

Volumetric Method for the Determination of Alpha-Cellulose

Procedure

Approximately 1 gram of oven-dry cellulose obtained from the previously described chlorination method or of air-dry lignin-free pulp, the moisture content of which has been previously determined on separate

duplicate samples is accurately weighed in a weighing bottle and transferred to a 250-ml. Pyrex beaker. Twenty-five ml. of a 17.5 percent (by weight) carbonate-free sodium hydroxide solution (see Note M) cooled to 20° C. are measured in a small graduate. Ten ml. of this solution are added to the pulp in the beaker maintained at 20° C. in a water bath and allowed to stand for 5 minutes. With a short glass rod, the end of which has been flattened to form a small disk, the material is macerated for 10 minutes, during which interval the remaining 15 ml. of sodium hydroxide solution (20° C.) are added intermittently in 5 ml. portions. The beaker covered with a watch glass is allowed to remain in the water bath at 20° C. for an additional 30 minutes, making a total mercerization treatment of 45 minutes. Twenty-five ml. of distilled water (20° C.) are added to the alkali-cellulose mixture followed by thorough stirring. Forty-five minutes after commencement of the mercerization treatment the contents of the beakers are filtered by means of suction into a 30-ml. Jena 1bG3 fritted glass bottom crucible. The residue in the crucible is washed first with 100 ml. of 8.3 percent sodium hydroxide solution (20° C.) and finally with 250 ml. of distilled water (20° C.) by means of suction. The alkali insoluble or alpha-cellulose is removed from the alundum crucible with a pointed glass rod and is placed in a 250 ml. beaker. The filtrate is used for the determination of beta- and gamma-celluloses. The alpha-cellulose is dissolved in approximately 30 ml. of 72 percent (by weight) sulfuric acid, is transferred to a 100 ml. graduated flask by washing successively with portions of the acid, and is filled with acid to the graduation mark. After thoroughly mixing a 10 ml. aliquot is pipetted into a 250-ml. Pyrex beaker, to which is added 10 ml. of standard dichromate solution and approximately 60 ml. of a solution not stronger than 72 percent (by weight) of sulfuric acid. The oxidizing mixture is boiled gently for exactly 5 minutes, is cooled in ice and the excess dichromate is titrated with ferrous ammonium sulfate solution as described in the section under the standardization of the potassium dichromate solution.

The percentage of alpha-cellulose in the oven-dry sample of cellulose or pulp is calculated as follows:

$$\frac{10 \times \frac{x - y}{x} \times 10 \times Z}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of alpha-cellulose,}$$

where x is the volume in cubic centimeters of Mohr's salt ($\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) solution equivalent to 10 ml. of potassium dichromate solution; y is the volume in ml. of Mohr's salt solution used in back titration of a 10-ml. aliquot or one-tenth of the original solution of alpha-cellulose dissolved in 72 percent of sulfuric acid; Z is the weight in grams of cellulose oxidized with 1 ml. of potassium dichromate solution. (See section on standard solutions.)

The Determination of Beta- Plus Gamma-Cellulose

The 350-ml. alkaline filtrate containing the beta- and gamma-cellulose, remaining from the insoluble or alpha-cellulose determination, is diluted to exactly 400 ml. This solution is divided into two equal parts. One 200-ml. portion, which is left alkaline, is diluted to 250 ml. in a graduated flask and is used for the determination of the beta- plus gamma-celluloses. A 25-ml. portion of this solution is pipetted into a 250-ml. beaker. To it are added 5 ml. of the standard dichromate solution and 60 ml. of 72 per-cent (by weight) sulfuric acid. The contents of the beaker are boiled for exactly 5 minutes, cooled in ice, and titrated as described under the alpha-cellulose determination. From this titration the sum of the per-centages of the beta- and gamma-celluloses is calculated as follows:

$$\frac{5 \times \frac{B-A}{B} \times 20 \times Z}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of beta- plus gamma-celluloses,}$$

where B is the volume in ml. of Mohr's salt solution equivalent to 5 ml. of the potassium dichromate solution; A is the volume in ml. of Mohr's salt solution used in the back titration of one-tenth of the alkaline solution of beta- and gamma-cellulose, and Z is the weight in grams of cellulose oxidized with 1 ml. of potassium dichromate solution.

The Determination of Gamma-Cellulose

The remaining 200 ml. of the alkaline filtrate from the alpha-cellulose determination is acidified with a 10 percent sulfuric acid solution using 1 drop of dilute methyl orange as an indicator, adding 5 ml. of this acid in excess and diluting to 250 ml. in a graduated flask. This procedure almost immediately precipitates the beta-cellulose. The flask is allowed to stand several hours, until the beta-cellulose coagulates and settles to the bottom. A 25-ml. portion of the supernatant liquid is pipetted from the flask and is treated as described under the determination of beta- plus gamma-celluloses. From this determination the percentage of gamma- or soluble cellulose is calculated as follows:

$$\frac{5 \times \frac{B-G}{B} \times 20 \times Z}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of gamma-cellulose,}$$

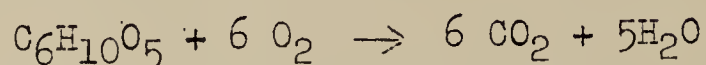
where B is the volume in ml. of Mohr's salt solution equivalent to 5 ml. of potassium dichromate solution; G is the volume in ml. of Mohr's salt solution used in back titration of gamma-cellulose, and Z is the weight in grams of cellulose oxidized with 1 ml. of potassium dichromate solution.

The Determination of Beta-Cellulose

The percentage of beta-cellulose is obtained by subtracting the percentage of gamma-cellulose from that of the beta- plus gamma-celluloses.

Standard Solutions for the Volumetric Determination of the Celluloses

Theoretically, cellulose is decomposed upon oxidation with potassium dichromate in sulfuric acid solution as follows:



Ninety grams of chemically pure potassium dichromate are dissolved in 1 liter of distilled water.

One hundred and fifty-nine and nine-tenths (159.9) grams of chemically pure ferrous ammonium sulfate (Mohr's salt) are made up to 1 liter with distilled water, containing 10 ml. of 10 percent (by weight) sulfuric acid to prevent hydrolysis and avoid the formation and separation of basic salts.

The potassium dichromate solution is standardized against either Cross and Bevan cellulose obtained from wood pulp or cotton.

Approximately 1 gram of cellulose (not corrected for ash) dried to constant weight at 105° C. is taken from a weighing bottle and placed in a 250-ml. beaker. This is triturated with 30 ml. of 72 percent (by weight) sulfuric acid and allowed to stand until solution is complete. The sulfuric acid solution is transferred to a 100-ml. graduated flask. The beaker is washed several times with 72 percent sulfuric acid to insure complete removal of the dissolved cellulose. The flask is filled to the graduation mark with 72 percent sulfuric acid and the contents are thoroughly mixed. To a 10-ml. portion of the dissolved cellulose pipetted into a 250-ml. beaker, 10 ml. of potassium dichromate solution and approximately 60 ml. of 72 percent (by weight) sulfuric acid are added. The solution in the beaker is boiled for exactly 5 minutes, is cooled in ice, and is titrated with ferrous ammonium sulfate solution using potassium ferricyanide as the indicator. The titration is conducted in the usual way and the point where a drop of the titrated solution gives a blue color with a drop of the indicator is taken as the end point of the titration. The relative value of the ferrous ammonium sulfate solution to the dichromate solution is established by titrating a 10-ml. portion of potassium dichromate solution with ferrous ammonium sulfate solution, using potassium ferricyanide as the indicator. From these values the cellulose equivalent of the dichromate solution is calculated as follows:

$$\frac{\text{Weight of cellulose taken}}{\text{ml. K}_2\text{Cr}_2\text{O}_7 \text{ used in oxidation}} = \frac{\text{Grams cellulose per ml. of K}_2\text{Cr}_2\text{O}_7 \text{ solution}}{Z}$$

Copper Number

The copper number of cellulose and pulp is defined as the number of grams of metallic copper in the cuprous oxide resulting from the reduction of the copper sulfate by 100 grams of the fibrous material.

The following method⁴⁷ constituting essentially the Braidy modification of the original Schwalbe method, with modifications for its adaptation to pulps and papers by Scribner and Brode and by Burton and Rosch is the Tentative Standard of the Technical Association of the Pulp and Paper Industry.⁴⁸ The method is suitable for cellulose, all pulps, and papers, excepting those containing such reducing agents as sulfides, though its principal use is for the evaluation of pulps free from unbleached fibers, groundwood, or other highly lignified fibers.

Reagents

A. Copper sulfate solution: Dissolve 100 grams of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in distilled water and dilute to exactly 1 liter (Note 0).

B. Carbonate-bicarbonate solution: Dissolve 350 grams of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) crystals or 129 grams of anhydrous Na_2CO_3 , and 50 grams of sodium bicarbonate (NaHCO_3) in distilled water and dilute to exactly 1 liter.

C. Molybdophosphoric acid: Dissolve 100 grams of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$) in a mixture of 275 ml. of conc. H_2SO_4 and 1.75 liters of distilled water.

D. Sodium carbonate solution: An approximately 5 percent solution of Na_2CO_3 in distilled water.

E. 0.05 normal potassium permanganate solution: Dissolve 1.5815 grams of KMnO_4 in exactly 1 liter of distilled water.

Procedure

Approximately 1.5 grams of cellulose or fluffed² pulp, the moisture and ash content of which have been determined on separate samples, are carefully weighed in a weighing bottle and transferred to a 125-ml. Erlenmeyer flask. Immediately before use 5 ml. of solution A are added to 95 ml. of solution B and the mixture, brought to a boil in 2 minutes, is poured over the 1.5-gram sample in the Erlenmeyer flask. The material is stirred with a glass rod to distribute the fibers and remove air bubbles, after

⁴⁷Schwalbe, C. G. "Die Chemie der Cellulose," 625 (1911).

Peters, A. W. J. Am. Chem. Soc. 34, 422 (1912).

Clibbens and Geake. Jr. Text. Inst. 15, T31 (1924).

Scribner and Brode. Technologic Paper No. 354, Natl. Bureau of Standards.

Burton and Rosch. Bureau of Standards J. of Research R.P.295, April 1934.

⁴⁸See T.A.P.P.I. Methods Nos. T-215 and 430-m38.

which the flask is covered with a loosely fitting glass stopper and submerged in a steam bath at atmospheric pressure, maintaining the temperature of the material in the flask at $100^{\circ}\text{C.} \pm 1^{\circ}\text{C.}$ The flask is allowed to remain in the steam bath for 3 hours with occasional shaking to redistribute any fibers tending to float to the surface. After 3 hours of treatment the contents of the flask are filtered on an ashless filter paper in a 7.5-cm. Büchner funnel using suction, washed first by flooding with 100 ml. of 5 percent sodium carbonate solution at 20°C. , and then by again flooding with 250 ml. of hot distilled water (95°C.), discarding the filtrates. The fibers and filter paper are transferred to a small beaker and 25 ml. of solution C are added and the whole mixed by maceration with a glass rod. The contents of the beaker are again filtered on a filter paper in a Büchner funnel and washed thoroughly with cold water until the blue molybdenum color is removed from the fibers. The filtrate is diluted to approximately 700 ml. and titrated to a faint pink color with standard 0.05 normal potassium permanganate solution.

The copper number is calculated to the nearest tenth of 1 percent according to the following equation:

$$\text{Copper number} = \frac{6.36 \times \text{ml. KMnO}_4 \times N}{W}$$

where N is the normality of the potassium permanganate solution and W is the weight of the oven-dry test specimen corrected for its ash content.

Note:

0.--The amount of solution A specified is sufficient for a copper number not greater than 6. This figure is seldom exceeded except in pulps containing highly lignified fibers, such as groundwood, or in pulps which have deteriorated considerably. If the copper number exceeds 6, the amount of solution A should be increased to 10 ml. and the amount of solution C to 50 ml. or as much as may be necessary, always retaining the specified ratio between all the solutions.

Permanganate Number of Pulp

The permanganate number⁴⁹ of pulp is defined as the number of milliliters of tenth normal potassium permanganate solution (0.1 N. KMnO_4) which reacts with 1 gram of oven-dry material under certain specified conditions. The following method is the tentative standard of the Technical Association of the Pulp and Paper Industry.

⁴⁹Niles, R. H. Paper Trade J. 98 (11), 34 (March 15, 1934).
See also Method No. T-214-m-37, Tentative Standard of the T.A.P.P.I.

The permanganate number may be converted into other terms, such as chlorine number, or percentage bleach requirement used to denote the relative hardness or bleachability of a pulp.

The method may be used on all ordinary types and grades of pulp sampled in any moisture condition or concentration and at any stage of processing.

Reagents

Potassium permanganate solution, 0.1 normal accurate to $\pm 0.0005N$.

Sodium thiosulphate solution, 0.1 normal accurate to $\pm 0.0005N$.

Potassium iodide solution, approximately normal, 166 grams of potassium iodide per liter.

Sulfuric acid, approximately 4 normal. Add 106 ml. of concentrated H_2SO_4 to about 500 ml. of cold water and dilute to 1 liter.

Starch indicator solution.

Procedure

Approximately 1 gram of pulp, oven-dry basis, (Note P) is weighed to the nearest 0.01 gram, disintegrated in a beaker with a measured quantity (50 to 400 ml.) of distilled water (Note Q), and treated for exactly 5 minutes at $25^\circ C$. with a 0.03 normal potassium permanganate solution acidified to 0.133 normal with sulfuric acid (Note R). The amount of permanganate to be added depends upon the degree of delignification of the test specimen.

For pulps of average bleachability, 25 ml. of 0.1N potassium permanganate solution, 25 ml. of sulfuric acid, and 700 ml. of distilled water are used to give a total volume of 750 ml., the concentration of which is 0.03 N . $KMnO_4$ and 0.133 N . H_2SO_4 . For pulps of higher or lower bleachability, proportionate quantities of 0.1N potassium permanganate, 4N sulfuric acid, and distilled water are employed, but the concentration of the reaction mixture should always be 0.03 potassium permanganate and 0.133 N . H_2SO_4 .

Having estimated the approximate quantity of permanganate to be used, this amount of 0.1N potassium permanganate solution and a like amount of 4N sulfuric acid are measured into a small beaker. The quantity of distilled water required to dilute the mixture to N/300 permanganate, less any water which may have been already used in disintegrating the test specimen, is calculated, accurately, measured, and added to the beaker containing the sulfuric acid. The temperature is adjusted so that the mixture of all constituents will be $25^\circ C. \pm 1^\circ C$. The disintegrated pulp sample in the reaction beaker is placed under the stirrer and the sulfuric acid-water mixture added, reserving about 10 ml. of the mixture for rinsing the beaker containing the permanganate. After starting the stirrer the permanganate is

quickly added, rinsing the beaker with the remainder of the sulfuric acid-water mixture. The reaction is allowed to proceed for exactly 5 minutes, during which period the pulp mixture is stirred at the rate of 500 r.p.m. At the end of this time the reaction is stopped by the addition of 5 ml. of potassium iodide solution, stopping the stirrer.

The potassium permanganate unconsumed by the pulp releases a proportionate amount of iodine which is titrated with tenth normal sodium thiosulfate, using the starch solution at the end of the titration as the indicator. The titration is made in the reaction beaker without removal of the fibers.

The permanganate number of the pulp is obtained by subtracting the number of milliliters of 0.1 normal thiosulfate used in the back titration from the number of milliliters of 0.1 normal permanganate added originally to the pulp and dividing the difference by the weight of oven-dry test specimen.

The number of milliliters of 0.1 normal potassium permanganate consumed by 1 gram of moisture-free pulp is reported as the permanganate number. Duplicate tests should agree within 0.5 ml.

According to the author⁴⁹ the chlorine number of the pulp may be calculated from the permanganate number by the use of certain factors.

Note:

P.--The test specimen may be in any form of dry or slush pulp, but should be representative of the entire lot of material. The moisture content of the pulp should be determined on a separate sample. If the pulp is sampled in slush form, it should be filtered and washed thoroughly with warm water on a Büchner funnel before weighing out or drying the test specimen.

Q.--If the material is disintegrated by hand with a glass rod the smaller quantity of water is added, whereas, if disintegration is accomplished with a stirrer the larger quantity of water is more advantageous.

R.--All conditions of the test specified should be rigidly followed, allowing no more than the following tolerances:

Weight of test specimen.....	1.00 gram, ± 0.02 gram
Temperature of the reaction.....	25° C., $\pm 1^\circ$ C.
Time of reaction.....	5 minutes ± 20 seconds
Permanganate concentration.....	0.029 to 0.031 normal -- (25 ml. ± 1 ml. 4N sulfuric acid to 25 ml. 0.1 normal potassium permanganate).

Acid Hydrolysis²

This method furnishes a means of measuring the acetyl groups ($\text{CH}_3\text{CO}-$), although it is not certain that all the acetic acid obtained is formed by the hydrolysis of the acetyl groups.

Approximately 2 grams of air-dry pulp or sawdust, the moisture content of which has been previously determined, or of oven-dry material are placed in a 250-ml. Erlenmeyer flask and 100 ml. of approximately 2.5 per-cent sulfuric acid is added. The flask is connected with a reflux condenser and the contents are boiled gently 3 hours and are then allowed to cool. The interior of the condenser is washed down with a little distilled water (Note S) and the contents of the flask are transferred to a 250-ml. graduated flask. Distilled water free from carbon dioxide is added up to the graduation mark, the solution is allowed to stand several hours with frequent shaking and is then filtered.

A wide-mouthed, round-bottomed, 750-ml. flask is provided with a rubber stopper containing: (1) a dropping funnel; (2) a glass tube drawn out to a capillary, closed with a rubber tube and pinchcock, and extending to the bottom of the flask; and (3) a Kjeldahl connecting bulb-tube. An ordinary condenser is used, to the end of which is attached a receiver consisting of a 500-ml. distilling flask cooled with a stream of water and connected with a manometer and a suction pump.

A few pieces of pumice are placed in the boiling flask to which is added 200 ml. of the filtrate from the acid hydrolysis (in the case of hardwoods use 100 ml.). The flask is heated in an oil bath maintained at 85°C ., while the pressure is reduced to 40 or 50 mm. of mercury. When the residue in the flask is reduced by distilling to about 20 ml., distilled water is added through the dropping funnel, drop by drop, at the same rate that distillation takes place. When 100 ml. of solution have been distilled over, the distillate is titrated with 0.1N sodium hydroxide, using phenolphthalein as the indicator. If (a) 200 ml. or (b) 100 ml. of solution were taken for distillation, the number of ml. of sodium hydroxide used is multiplied by (a) $5/4$, or (b) $5/2$, respectively, and is calculated as acetic acid. The method of calculation follows:

$$\frac{\text{ml. NaOH} \times F \times N \times 0.0600}{\text{Oven-dry weight of sample}} \times 100 = \text{Percentage of acetic acid,}$$

where 0.0600 = the weight of acetic acid equivalent to 1 ml. of normal sodium hydroxide; $F = 5/4$ if 200 ml. of solution were taken for distillation; $F = 5/2$ if 100 ml. of solution were taken for distillation; N = normality of sodium hydroxide.

Note:

S.--All distilled water used in this determination should be boiled previous to use in order to expel carbon dioxide.

Determination of Methoxyl Groups in Wood and Pulp

The methoxyl groups are determined according to the method of Zeisel.⁵⁰ The principle of the determination depends upon the formation of methyl iodide when the substance to be examined is heated with hydriodic acid. The methyl iodide is swept from the reaction flask by a current of carbon dioxide into absorption vessels containing an alcoholic 0.1N silver nitrate solution, the methyl iodide decomposing with the formation of silver iodide. For a small number of determinations it is preferable to weigh the silver iodide directly, while for a large number of determinations the volumetric method may be preferable.

Gravimetric Method

Reagents

A. Alcoholic silver nitrate:

The silver nitrate solution is prepared by dissolving 17 grams of the chemically pure salt in 50 ml. of distilled water and making up to a liter with previously purified 95 percent ethyl alcohol. The aldehydes are removed from the alcohol as follows: Dissolve 1.5 grams of silver nitrate in 3 ml. of distilled water, add the resulting solution to 1 liter of 95 percent ethyl alcohol, and shake well. Dissolve 3 grams of sodium hydroxide in about 15 ml. of 95 percent ethyl alcohol. Warm this solution gently, cool, and add to the main solution. Shake the mixture well, allow it to settle for several days, siphon off the clear solution, and distill, adding a piece of pumice to keep the liquid from bumping.

B. Hydriodic acid:

If the acid, as purchased, is not water-white and of sufficient specific gravity (1.70), it must be redistilled. The acid is placed in a distillation flask with a few grams of red phosphorous. The sides of the flask are protected from overheating by setting the flask on a piece of asbestos, containing a hole cut in the center sufficiently large to permit heating of only the liquid in the flask. The distillate coming over between 124° - 130° C. is collected and stored in a glass-stoppered brown bottle.

⁵⁰Zeisel; Monatsh, 6, 989 (1885); 7, 406 (1886).

R. J. Manning and M. Nierenstein, Ber. 46, 3983 (1913).

Fritz Weishut, Monatsh 33, 1165-12 (1912).

A. Klemene, Monatsh 34, 901-12 (1913).

Benedict and Bamberger, Monatsh 15, 509 (1894).

Apparatus

The apparatus shown in Figure 3 may be employed for the determination of the methoxyl groups. Essentially the apparatus consists of a 50-ml. reaction flask (B) connected by a ground-glass connection to a 24-inch condenser (C), the top of which (Fig. 3) forms a trap (D), which contains a water suspension of red phosphorous, and an absorption apparatus (E).

Procedure

Approximately 0.3 gram of oven-dry sawdust or 0.5 gram of pulp is accurately weighed into the digestion flask (B) and 15 ml. of redistilled hydriodic acid (sp. gr. 1.70) are added. The reaction flask is heated in a glycerin or oil bath to 130° C.

The temperature in the condenser (C) is maintained at 45°-55° C. by means of the preheater (X) through which water is kept flowing constantly by connection with a water tap. A water suspension of red phosphorous is placed in trap (D), Figure 3. The methyl iodide is absorbed in 35 ml. of 0.1N silver nitrate placed in the absorption apparatus (E). As soon as all connections are made, a current of washed, dry CO₂ gas is passed through the apparatus at the rate of 50 to 60 bubbles per minute. The heating is continued until the silver nitrate solution, at first milky, has become clear; this requires from 1-1/2 to 2 hours. The contents of the absorption apparatus (E) are washed into a beaker, made up to 300 ml. and heated on a steam bath until the contents have evaporated to 50 ml. Ten ml. of concentrated nitric acid are added and the solution is boiled to decompose phosphides. After cooling, the silver iodide is filtered on a tared Gooch filter, washed with hot water containing a little nitric acid, dried for 1-1/2 hours at 105° C., cooled in a desiccator and weighed as silver iodide. The methoxyl is calculated as a percentage of the oven-dry weight of the sample according to the following equation:

$$\text{Percent methoxyl} = 13.2 \times \frac{\text{Weight AgI}}{\text{Weight of oven-dry sample}}$$

Volumetric Method

Solutions

Alcoholic silver nitrate solution: See gravimetric method.

Potassium thiocyanate solution: This solution is made by dissolving approximately 10 grams of the chemically pure salt in distilled water and making up to 1 liter.

The silver nitrate and the potassium thiocyanate solutions are standardized as follows: A known weight (0.5 gm.) of chemically pure dry sodium chloride is made up to 250 ml. with distilled water; to 25 ml. portions of the salt solution, known volumes (about 15 ml.) of the alcoholic silver

nitrate solution are slowly added, with constant stirring. The beakers are placed in a steam bath and heated until all the alcohol is expelled. A few drops of nitric acid are added, the precipitated silver chloride filtered off, washed, and the filtrate titrated with the solution of potassium thiocyanate, by adding 5 ml. of a saturated solution of ferric alum acidified with nitric acid as the indicator. An equal volume of silver nitrate solution, to which no sodium chloride has been added, is also titrated with the potassium thiocyanate solution. The difference in the volumes of the potassium thiocyanate required in the two titrations is the equivalent of the sodium chloride added, expressed in terms of silver nitrate. From the weight of the sodium chloride employed and the volumes of silver nitrate and potassium thiocyanate solutions can be calculated as follows:

g = weight in grams sodium chloride in 15 ml. of solution.
 x = ml. potassium thiocyanate equivalent to 25 ml. silver nitrate solution.
 Then 25 ml. silver nitrate solution is equivalent to the weight (g) of sodium chloride + y ml. of potassium thiocyanate.
 xy = ml. potassium thiocyanate equivalent to (g) grams of sodium chloride.

Procedure

The same procedure as previously described for the gravimetric method is employed. After the methyl iodide has been absorbed in the 35 ml. of 0.1N silver nitrate solution as before, the contents of the absorption apparatus are washed into a beaker, made up to 300 ml. with distilled water and heated on a steam bath until the contents have evaporated to 50 ml. Ten ml. of concentrated nitric acid are added, the silver iodide filtered off, washed with hot water containing a little nitric acid and the silver nitrate remaining in the filtrate is titrated with the standard 0.1N potassium thiocyanate solution. One ml. of 0.1N silver nitrate is equal to 0.0031 grams of methoxyl (CH_3O). The percentage of methoxyl is calculated as follows:

x = ml. potassium thiocyanate equivalent to 35 ml. silver nitrate.
 y^1 = ml. potassium thiocyanate used in back titration of silver nitrate after reacting with methyl iodide.
 N = normality of the potassium thiocyanate solution.

$$\frac{(x-y^1) \times N \times 0.031}{\text{Weight of oven-dry sample}} \times 100 = \text{Percentage of methoxyl in the material.}$$

The Determination of Pentosans⁵¹ in Wood or Pulp

When substances containing pentosans are distilled with 12 percent hydrochloric acid solution, furfural is formed. The furfural in the

⁵¹For a review of the literature and bibliography on the Determination of Pentosans see Pervier & Gortner, Ind. Eng. Chem. 15, 1167, 1255 (1923).

distillate may be precipitated with phloroglucine as furfural phloroglucide, which can be determined gravimetrically. Although the method is empirical, results can be closely duplicated if all conditions, such as concentration of acid, rate of distillation, etc., are carefully observed.

Apparatus

The apparatus in Figure 4 consists of (1) a 300-ml. ordinary, round-bottom flask of the wash bottle type, to the glass stopper of which is fused an outlet tube and a separatory funnel; (2) a water-cooled glass condenser; and (3) a graduated cylinder provided with a funnel.

Solutions

Hydrochloric acid solution: A 12 percent by weight of hydrochloric acid, sp. gr. 1.06.

Phloroglucinol solution: Eleven grams of phloroglucinol are heated in a beaker with 300 ml. of 12 percent hydrochloric acid. When the solution is complete, it is diluted with 12 percent hydrochloric acid to 1,500 ml. Before using, the solution should stand for a week to allow any diresorcin, which vitiates the determination, to crystallize out.

Procedure

Two grams of oven-dry pulp or 1.5 grams of sawdust are placed in the 300 ml. reaction flask provided with a separatory funnel and attached to a condenser as shown in Figure 4. A small piece of paraffin and a few glass beads are placed in the flask to which is added approximately 100 ml. of 12 percent chemically pure hydrochloric acid (sp. gr. = 1.06). The contents of the flask are distilled at the maximum rate of 30 ml. in 10 minutes. (More rapid distillation gives low results.) The distillate is passed through a small filter before entering the receiver. As soon as 30 ml. of distillate are collected 30 ml. of 12 percent hydrochloric acid are added to the distillation flask and the distillation is continued in this manner until 360 ml. of distillate are collected. To the total distillate are added 40 ml. of filtered phloroglucinol solution that has been prepared at least a week previously. Upon addition of the phloroglucinol solution, the distillate soon turns greenish black. After standing 16 hours (Note T) the furfural phloroglucide will have settled to the bottom of the beaker. If a drop of the supernatant liquid gives a pink color with aniline hydrochloride paper (Note U) the precipitation of the furfural is incomplete.

A further amount of phloroglucine solution is then added and the beaker is again allowed to stand 16 hours. In no case so far in the analysis of wood or pulp of the size sample designated has it been necessary to use more than 40 ml. of phloroglucine solution.

The furfural phloroglucide suspension is filtered on a tared Gooch crucible having a thick asbestos mat, and the cake is washed with exactly 150 ml. of cold water. The crucible is dried for 4 hours in a water oven or for 2-1/2 hours in an air oven at 105° C., cooled in a stoppered weighing bottle, and weighed.

From the weight of the furfural phloroglucide obtained, the weight of pentosans present in the sample may be found from the following tables of Kröber and Tollens.⁵² The table for the calculations has a range for weights of phloroglucide between 0.030 and 0.300 gram. For weights of phloroglucide outside of these limits, Kröber⁵² gives the following formulae:

Kröber's Formulae

<u>Substance sought</u>	<u>Weight of phloroglucide less than 0.030 gram</u>
-------------------------	---

Furfural.....	$(a^* + 0.0052) \times 0.517$
Pentoses.....	$(a + 0.0052) \times 1.017$
Pentosans.....	$(a + 0.0052) \times 0.8949$

<u>Weight of phloroglucide 0.030 to 0.300 gram</u>
--

Furfural.....	$(a + 0.0052) \times 0.5185$
Pentoses.....	$(a + 0.0052) \times 1.0075$
Pentosans.....	$(a + 0.0052) \times 0.8866$

<u>Weight of phloroglucide exceeds 0.300 gram</u>

Furfural.....	$(a + 0.0052) \times 0.5180$
Pentoses.....	$(a + 0.0052) \times 1.0026$
Pentosans.....	$(a + 0.0052) \times 0.8824$

*a = The oven-dry weight in grams of furfural phloroglucide.

The pentosan content expressed as a percentage of the original oven-dry material is calculated from the following equation:

$$\frac{\text{Weight of pentosans}}{\text{Weight of oven-dry sample}} \times 100 = \text{Percentage of pentosans in the material.}$$

⁵²Abderhalden's "Handbuch der biochemischen Arbeitsmethoden" Vol 2, 137-154. J. Landw., 48, 379 (1900). Handbook of Sugar Analysis, Browne, 452. Methods of Analysis of the Association of Official Agricultural Chemists (1925), 121-458.

Krober's tables for the calculation of pentosans from furfural phloro-
glucide:

Phloro- glucide	Pentosans	Phloro- glucide	Pentosans	Phloro- glucide	Pentosans
0.030	0.0315	0.074	0.0706	0.118	0.1094
.031	.0324	.075	.0714	.119	.1103
.032	.0333	.076	.0722	.120	.1111
.033	.0341	.077	.0731	.121	.1120
.034	.0350	.078	.0740	.122	.1129
.035	.0359	.079	.0749	.123	.1138
.036	.0368	.080	.0758	.124	.1147
.037	.0377	.081	.0767	.125	.1156
.038	.0386	.082	.0776	.126	.1165
.039	.0395	.083	.0785	.127	.1174
.040	.0404	.084	.0794	.128	.1183
.041	.0413	.085	.0803	.129	.1192
.042	.0422	.086	.0812	.130	.1201
.043	.0431	.087	.0821	.131	.1210
.044	.0440	.088	.0830	.132	.1219
.045	.0448	.089	.0838	.133	.1227
.046	.0457	.090	.0847	.134	.1236
.047	.0466	.091	.0856	.135	.1244
.048	.0475	.092	.0865	.136	.1253
.049	.0484	.093	.0874	.137	.1262
.050	.0492	.094	.0883	.138	.1271
.051	.0501	.095	.0891	.139	.1280
.052	.0510	.096	.0899	.140	.1288
.053	.0519	.097	.0908	.141	.1297
.054	.0528	.098	.0917	.142	.1306
.055	.0537	.099	.0926	.143	.1315
.056	.0546	.100	.0935	.144	.1324
.057	.0555	.101	.0944	.145	.1333
.058	.0564	.102	.0953	.146	.1342
.059	.0573	.103	.0962	.147	.1351
.060	.0581	.104	.0971	.148	.1360
.061	.0590	.105	.0979	.149	.1369
.062	.0599	.106	.0988	.150	.1377
.063	.0608	.107	.0997	.151	.1386
.064	.0617	.108	.1006	.152	.1395
.065	.0625	.109	.1015	.153	.1404
.066	.0634	.110	.1023	.154	.1413
.067	.0643	.111	.1032	.155	.1421
.068	.0652	.112	.1041	.156	.1430
.069	.0661	.113	.1050	.157	.1439
.070	.0670	.114	.1059	.158	.1448
.071	.0679	.115	.1067	.159	.1457
.072	.0688	.116	.1076	.160	.1465
.073	.0697	.117	.1085	.161	.1474

Kröber's tables for the calculation of pentosans from furfural phloro-
glucide (continued)

Phloro- glucide	Pentosans	Phloro- glucide	Pentosans	Phloro- glucide	Pentosans
-----:-----		-----:-----		-----:-----	
0.162	0.1483	0.208	0.1887	0.254	0.2290
.163	.1492	.209	.1896	.255	.2299
.164	.1501	.210	.1904	.256	.2307
.165	.1510	.211	.1913	.257	.2316
.166	.1519	.212	.1922	.258	.2325
.167	.1528	.213	.1931	.259	.2334
.168	.1537	.214	.1940	.260	.2342
.169	.1546	.215	.1948	.261	.2351
.170	.1554	.216	.1957	.262	.2359
.171	.1563	.217	.1966	.263	.2368
.172	.1572	.218	.1974	.264	.2377
.173	.1581	.219	.1983	.265	.2385
.174	.1590	.220	.1992	.266	.2394
.175	.1598	.221	.2001	.267	.2403
.176	.1607	.222	.2010	.268	.2412
.177	.1616	.223	.2019	.269	.2421
.178	.1625	.224	.2028	.270	.2429
.179	.1634	.225	.2038	.271	.2438
.180	.1642	.226	.2046	.272	.2447
.181	.1651	.227	.2054	.273	.2456
.182	.1660	.228	.2063	.274	.2465
.183	.1669	.229	.2072	.275	.2473
.184	.1678	.230	.2081	.276	.2482
.185	.1686	.231	.2089	.277	.2490
.186	.1695	.232	.2097	.278	.2499
.187	.1704	.233	.2106	.279	.2508
.188	.1712	.234	.2115	.280	.2517
.189	.1721	.235	.2124	.281	.2526
.190	.1729	.236	.2132	.282	.2534
.191	.1738	.237	.2141	.283	.2543
.192	.1747	.238	.2150	.284	.2552
.193	.1756	.239	.2159	.285	.2561
.194	.1764	.240	.2168	.286	.2570
.195	.1773	.241	.2176	.287	.2578
.196	.1782	.242	.2185	.288	.2587
.197	.1791	.243	.2194	.289	.2596
.198	.1800	.244	.2203	.290	.2605
.199	.1808	.245	.2212	.291	.2614
.200	.1817	.246	.2220	.292	.2622
.201	.1826	.247	.2229	.293	.2631
.202	.1835	.248	.2238	.294	.2640
.203	.1844	.249	.2247	.295	.2649
.204	.1853	.250	.2256	.296	.2658
.205	.1861	.251	.2264	.297	.2666
.206	.1869	.252	.2272	.298	.2675
.207	.1878	.253	.2281	.299	.2684
				.300	.2693

Note:

T.--Boëdener and Tollens (J. Landw. 58, 232-7) have found that if the distillate containing the phloroglucine is heated to 80° to 85° C. and is then allowed to stand for 2 hours the precipitate of furfural phloroglucide can be filtered off without waiting for the solution to stand overnight. The method described in the text, however, is preferable.

U.--The aniline hydrochloride paper is conveniently prepared by dipping strips of filter paper into aniline hydrochloride solution. The latter is prepared by adding hydrochloric acid, drop by drop, to a mixture of equal parts of aniline and water until a clear solution is obtained.

Cuprammonium Disperse Viscosity of Pulp

The method described, consisting essentially of the Shirley Institute⁵³ procedure has been adopted by the Technical Association of the Pulp and Paper Industry for the determination of the viscosity of bleached and unbleached chemical pulps and rag stocks dispersed in cuprammonium solution.

Apparatus and Its Calibration

The viscosity tube shown in Figure 5, left, is used both for dissolving the pulp and for determining the viscosity of the solution. The tube, of heavy Pryex glass, has an internal diameter of 1.0 cm. and a total length of 27 cm. The capillary is 2.5 cm. long and 0.09 cm. inside diameter. The wide portion is etched with three rings, A, B, and C, at heights 24.2, 12.2, and 6.2 cm., respectively, above the flat end of the capillary. (The mark at B is optional, to be used with hard unbleached pulps. In this case the constant for the tube between the marks A and B should also be determined.)

The applicability of the procedure to pulps of widely varying viscosities is greatly improved by using tubes of different efflux rates for different pulps. The following efflux rates, determined with distilled water at 20° C., are specified:

	<u>Seconds</u>
Bleached pulp.....	15-25
Unbleached pulp and high-viscosity rag stock.....	10-15

The top of the tube is closed with a rubber stopper, carrying another capillary which has a ground-glass stopcock. The bottom capillary is

⁵³Clibbens and Geake. J. Textile Inst. 19, 77T (1928). TAPPI Method No. T206m.

closed with a rubber tube and clamp. Each tube has a wedge-shaped cylinder, Figure 5, top, the bottom of which is notched. The cylinder, made from 1/4" steel or Monel rod, is 2.5 cm. long.

The glass jacket, Figure 5, right, supports the viscosity tube in the water bath (Note V). The jacket is so constructed that it supports the tube on three glass points at the bottom and is a sliding fit at the top.

The volume of the tube is obtained as follows: The tube, containing the wedge, is filled with water, the rubber stopper (Note W) is put tightly in place and the excess water forced out through the capillary. The stop-cock is opened and the contents drained into a burette, noting the time in seconds for the meniscus to fall from line A to line C. Readings are made of the volume of the water delivered to the burette and the average of several determinations is taken as the volume of the tube.

The tube constants \underline{C} and \underline{k} are determined from the formula:

$$(1) \quad V = \frac{d}{C} \left(t - \frac{k}{t} \right),$$

where \underline{V} = viscosity in centipoises; \underline{d} = specific gravity of the solution; \underline{t} = time in seconds for meniscus to fall from line A to C; \underline{C} = tube constant; and \underline{k} = specific gravity constant.

The constant \underline{C} (Note X) is first determined with standard glycerine solution of approximately 1.21 sp. gr. (85 percent solution) at 20.0° C. The specific gravity must be accurately determined with a pycnometer. The viscosity may be obtained from a curve drawn from the following table. In this case constant \underline{k} may be disregarded, since the time of efflux is long. The formula then becomes

$$(2) \quad C = \frac{dt}{V},$$

from which the tube constant is calculated. The specific gravity constant \underline{k} is determined by repeating the operation with water at 20° C. and substituting for \underline{C} in formula (1) the value found above, as well as $d = 1$ and $V = 1$. The formula then becomes

$$(3) \quad k = t^2 - Ct$$

Viscosity of glycerine-water solutions
(International Critical Tables, Vol.5, p.23)

<u>Specific gravity at 20° C.</u>	<u>Viscosity in centipoises at 20° C.</u>
1.0000	1.009
1.1014	3.734
1.1699	15.360
1.1848	23.540
1.2057	49.670
1.2155	74.780
1.2240	110.800
1.2463	409.300
1.2568	871.700

Reagents

Cuprammonium solution: The cuprammonium solution should be freshly prepared at least every 2 months as follows: Clean copper turnings are placed in a glass tube 24 inches long and 4 inches in diameter surrounded with ice. (The turnings must be previously cleaned by washing in dilute hydrochloric acid.) Concentrated ammonium hydroxide (26-28 percent ammonia) containing 2 grams of cane sugar per liter is poured into the tube until nearly full. Air that has passed through a wash-bottle containing concentrated ammonium hydroxide is bubbled through the solution for several hours, until the desired copper concentration is reached. The solution is analyzed for copper and ammonia, and the proper adjustments made. The copper concentration should be 14.8 to 15.2 grams per liter and the ammonia concentration should be 190 to 210 grams per liter.

The course of the reaction can be followed by estimating the copper content colorimetrically by comparing with a standard, both diluted 50-fold.

The copper and ammonia in the cuprammonium solution are determined as follows:

(a) Copper: Ten ml. of the cuprammonium solution are pipetted into a 250-ml. Erlenmeyer flask, and diluted with 25 ml. of water. The solution is boiled until no more ammonia is given off. Five ml. of nitric acid (1:1) are added and boiled till red fumes are expelled. Two ml. of bromine water are then added and boiled until the bromine is all expelled. The flask is next removed from the heat, diluted to 75 ml. of distilled water and ammonium hydroxide is added carefully until the solution becomes just alkaline (blue) but not more. A slight excess (4 or 5 ml.) of glacial acetic acid is added after which the flask is cooled to approximately 15° C., and 10 ml. of 30 percent potassium iodide solution added. The solution is then titrated with 0.1 N thiosulfate solution until the yellow color of free iodine is nearly gone, then starch indicator is added and the titration continued cautiously until, on the addition of another drop, the blue color due to free iodine disappears.

Calculation: Copper content of cuprammonium solution in grams per liter = ml. 0.1 N thiosulfate x 0.636.

(b) Ammonia: Two ml. of the cuprammonium solution are pipetted into 50 ml. of normal sulfuric acid solution, keeping the tip of the pipette beneath the surface of the liquid. The excess acid is titrated with normal sodium hydroxide, using methyl red indicator.

Calculation: Ammonia content of cuprammonium solution in grams per liter = (50-ml. sodium hydroxide) x 8.5-0.536 C, where C = copper concentration in grams per liter.

Care should be taken that no liquid adheres to the outside of the pipette before it is inserted into the acid solution. The correction factor (0.536C) is made for the alkalinity of the copper hydroxide.

Test Specimen

A representative sample of pulp in the air-dry condition is shredded by means of a mechanical shredder such as the Koerner type mill.³ The air-dry, shredded pulp is placed in a stoppered bottle and the moisture determined on a separate sample. The weight of air-dry pulp equivalent to 1 gram of oven-dry pulp for each 100 ml. of tube volume is calculated for each viscosity tube and the proper amount of sample is weighed out for the particular tube employed.

Procedure

The calculated weight of air-dry pulp to give a 1 percent solution of oven-dry pulp is accurately weighed in a stoppered bottle and rolled loosely into the form of a cigarette in a strip of hard surfaced paper such as glassine. The rolled pulp is moistened with 5 or 6 drops of water and slid from the paper into the viscosity tube. Cuprammonium solution is siphoned into the bottom of the tube through the rubber tubing until the tube is two-thirds full. The pulp roll is quickly broken up with the aid of a thin glass stirring rod. The remainder of the solution is added at the top, the glass rod is scraped clean, the stopper is inserted, and after forcing the excess solution through the capillary tube in the stopper the stopcock is closed.

The viscosity tube is wrapped in a black cloth and placed (Note Y) on a wheel rotating at the rate of 3 to 4 r.p.m., so that the metal wedge falls freely through the solution as the tube rotates.

After 15 hours rotation (over night) for the complete dispersion of the pulp, the tube is placed in a thermostat (Note W) at 20° C. until equilibrium is established. The rubber tubing is removed from the capillary and the tube placed in position in the jacket, which remains in the thermostat. The rubber stopper in the tube is then removed and the pulp solution is allowed to flow through the capillary. The time (t) in seconds required for the meniscus to pass between the marks A and C on the tube is noted and the viscosity of the solution is calculated from the formula:

$$(1) \quad V = \frac{d}{C} \left(t - \frac{k}{t} \right),$$

in which \underline{d} , the specific gravity of the pulp solution, is 0.96; \underline{C} and \underline{k} are constants. Simplifying the equation becomes:

$$(2) \quad V = C_1 \left(t - \frac{k}{t} \right)$$

$$\text{where } C_1 = \frac{0.96}{C}$$

Inspection will show when the expression $\frac{k}{t}$ may be disregarded, as is usually the case with unbleached pulps of high viscosity. After completion of the experiment the tubes should be cleaned by immersion in a 1 to 1 solution of nitric acid.

The results are reported in terms of centipoises and should represent the average of at least two tests. Duplicate samples should check within 2.0 percent on bleached pulps and 3.0 percent on unbleached pulps.

Note:

V.--For a number of determinations, it has been found convenient to have a series of jacket tubes placed in a thermostatically controlled water bath provided with a glass window on the side.

W.--The rubber stopper must be replaced periodically by a fresh one, determining the new volume each time.

X.--Mineral oil reference standards for the calibration of the viscosity tubes used in this method are commercially available. These reference standards are approximately 20 to 50 centipoises with a statement of the actual measurement within a tolerance of error of 0.5 centipoise.

Y.--Before placing the viscosity tube and contents on the rotating wheel the pulp should be well broken up so that the metal wedge will fall freely through the full length of the tube.

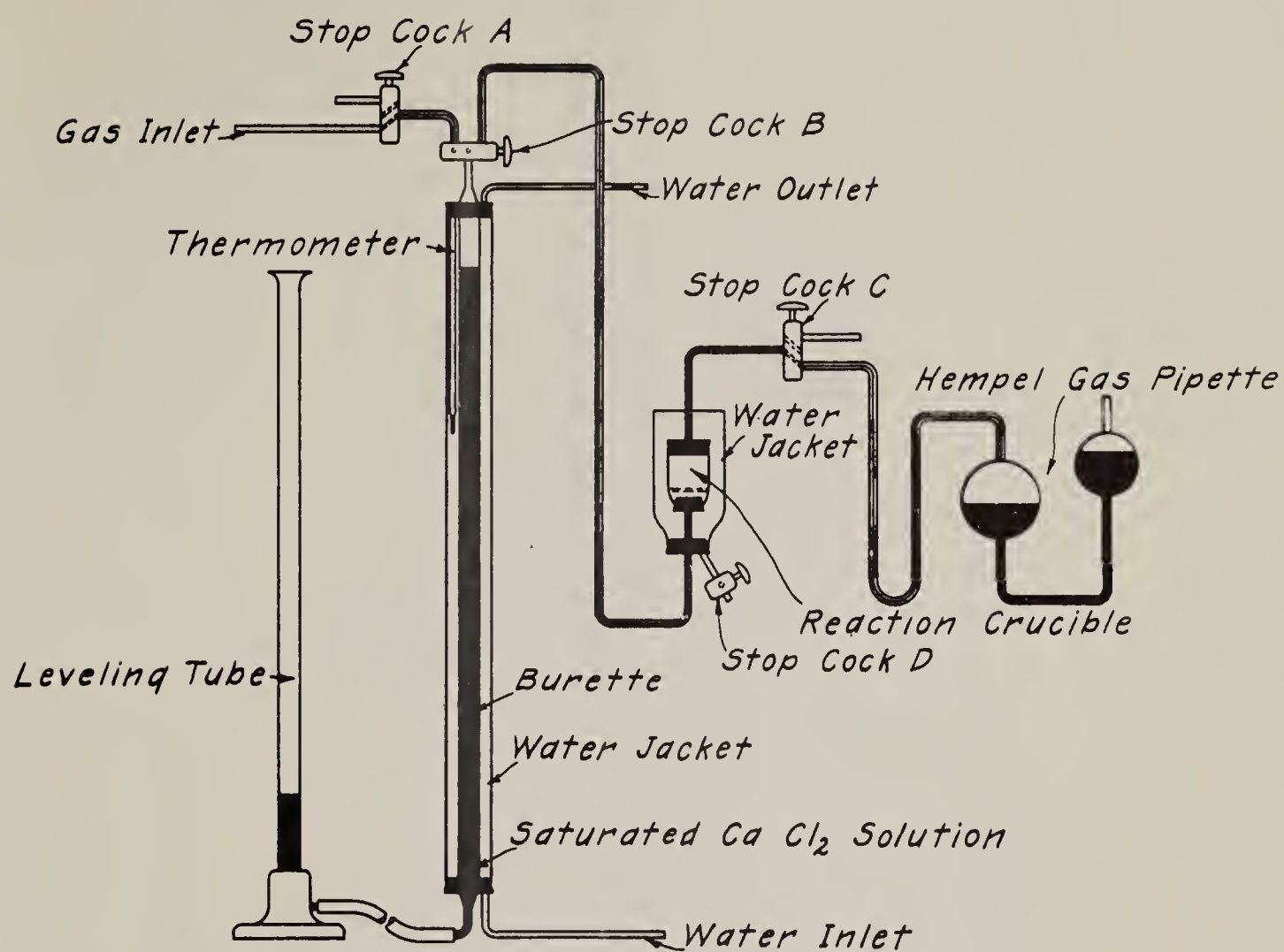


FIG.1-APPARATUS FOR THE DETERMINATION OF CHLORINE ABSORPTION IN THE ISOLATION OF CELLULOSE

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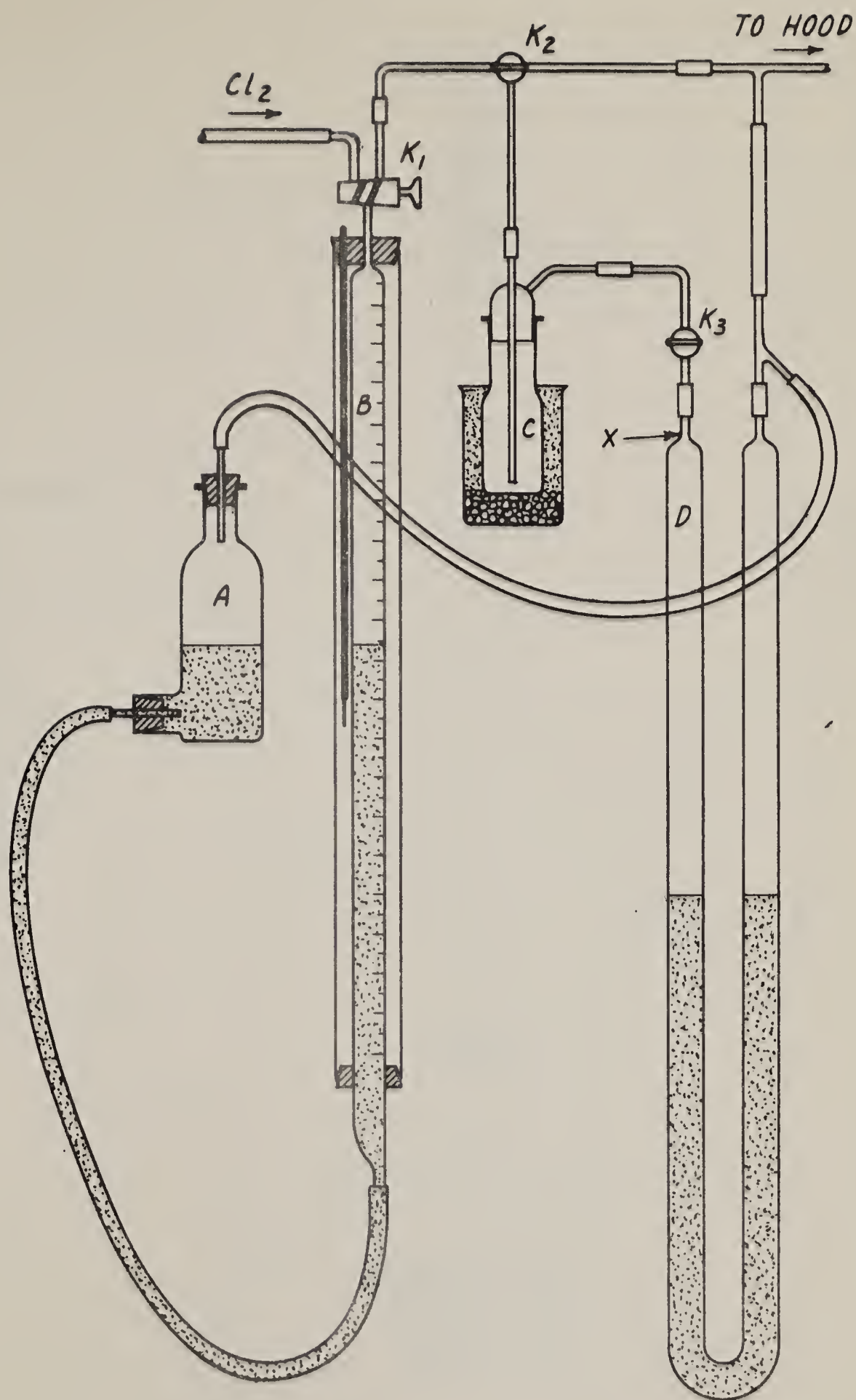


FIG. 2-APPARATUS FOR THE DETERMINATION OF
CHLORINE NUMBER OF PULPS

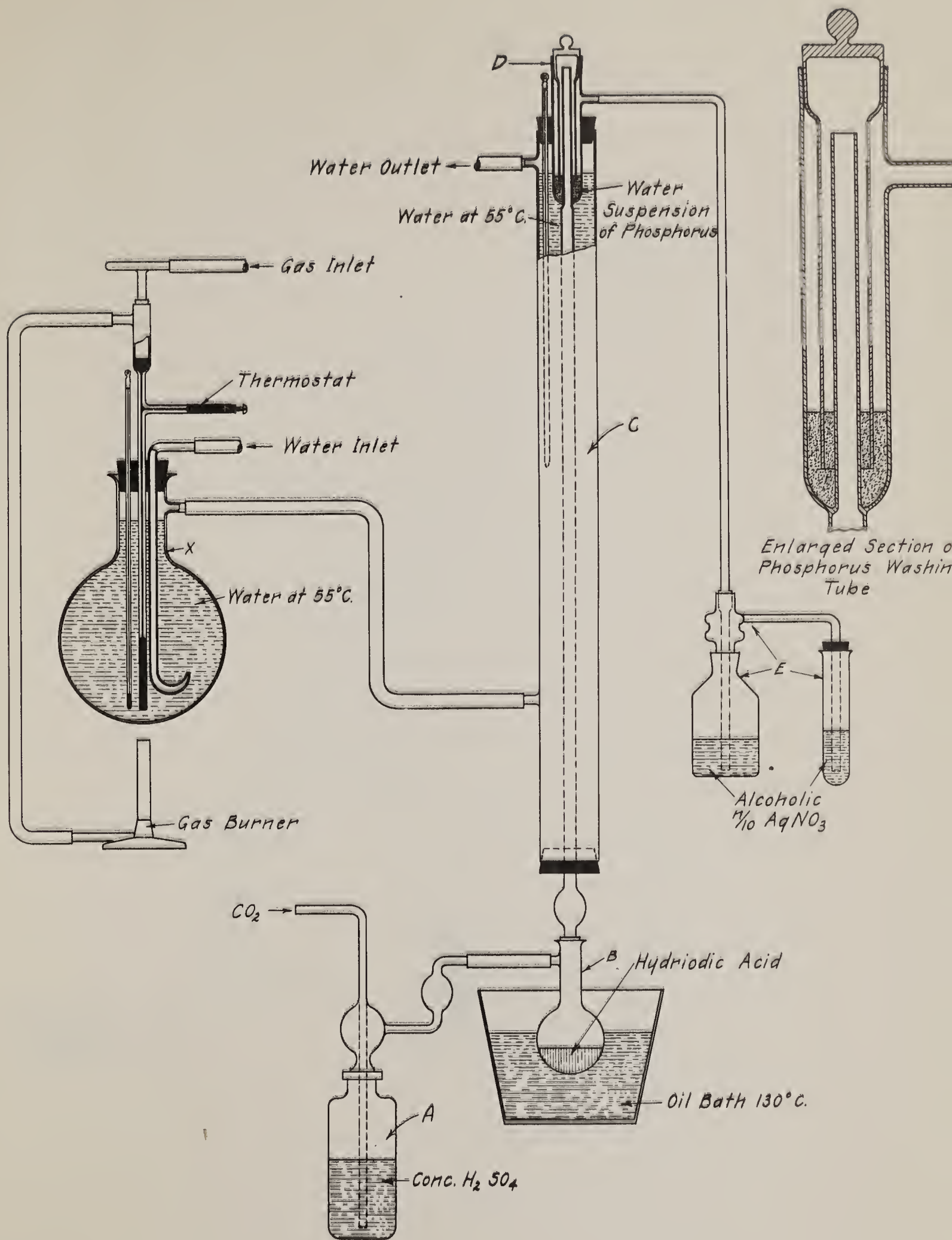


FIG. 3—APPARATUS FOR THE DETERMINATION OF METHOXYL GROUP

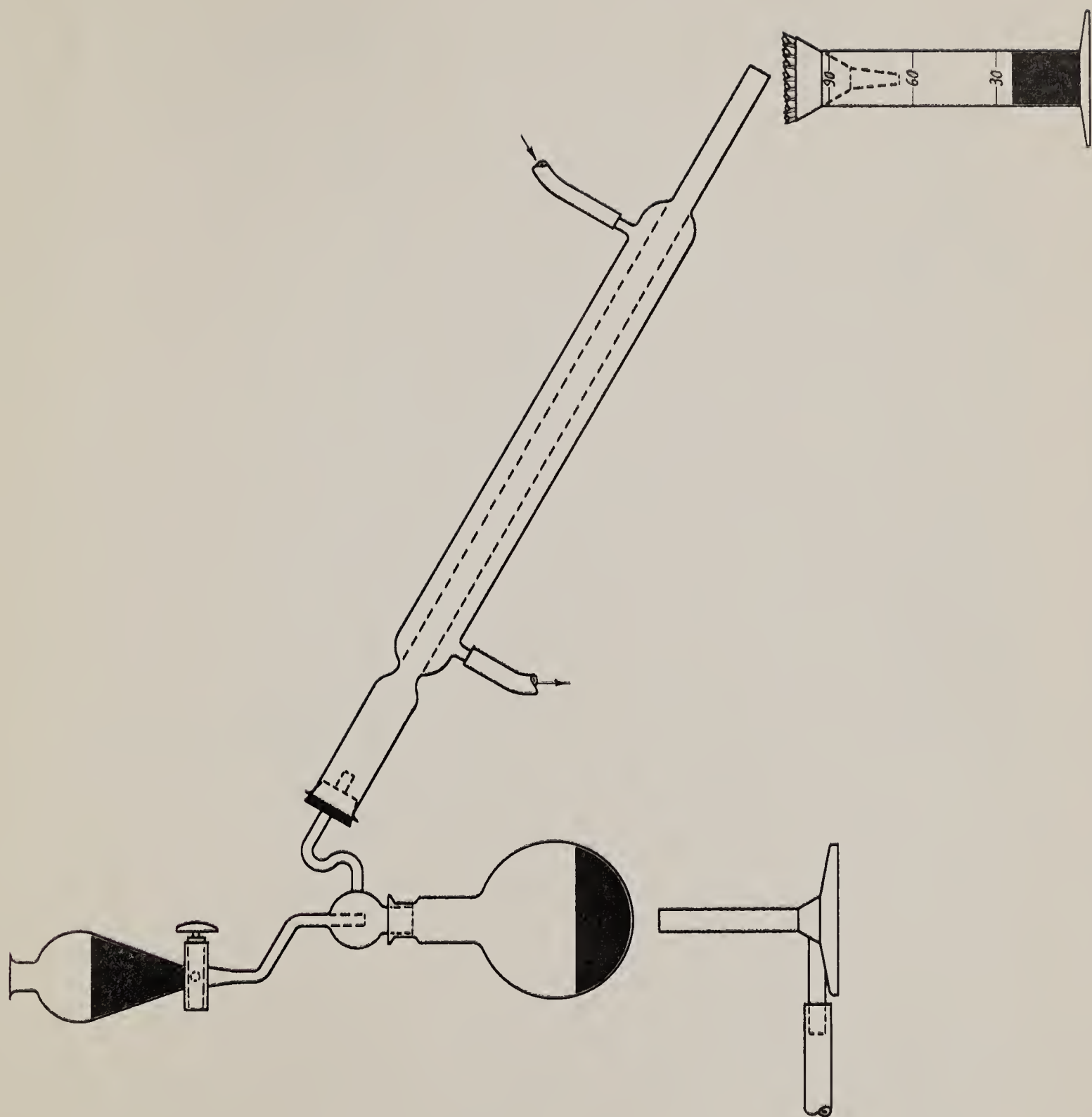


FIG. 4—APPARATUS FOR THE DETERMINATION OF PENTOSANS

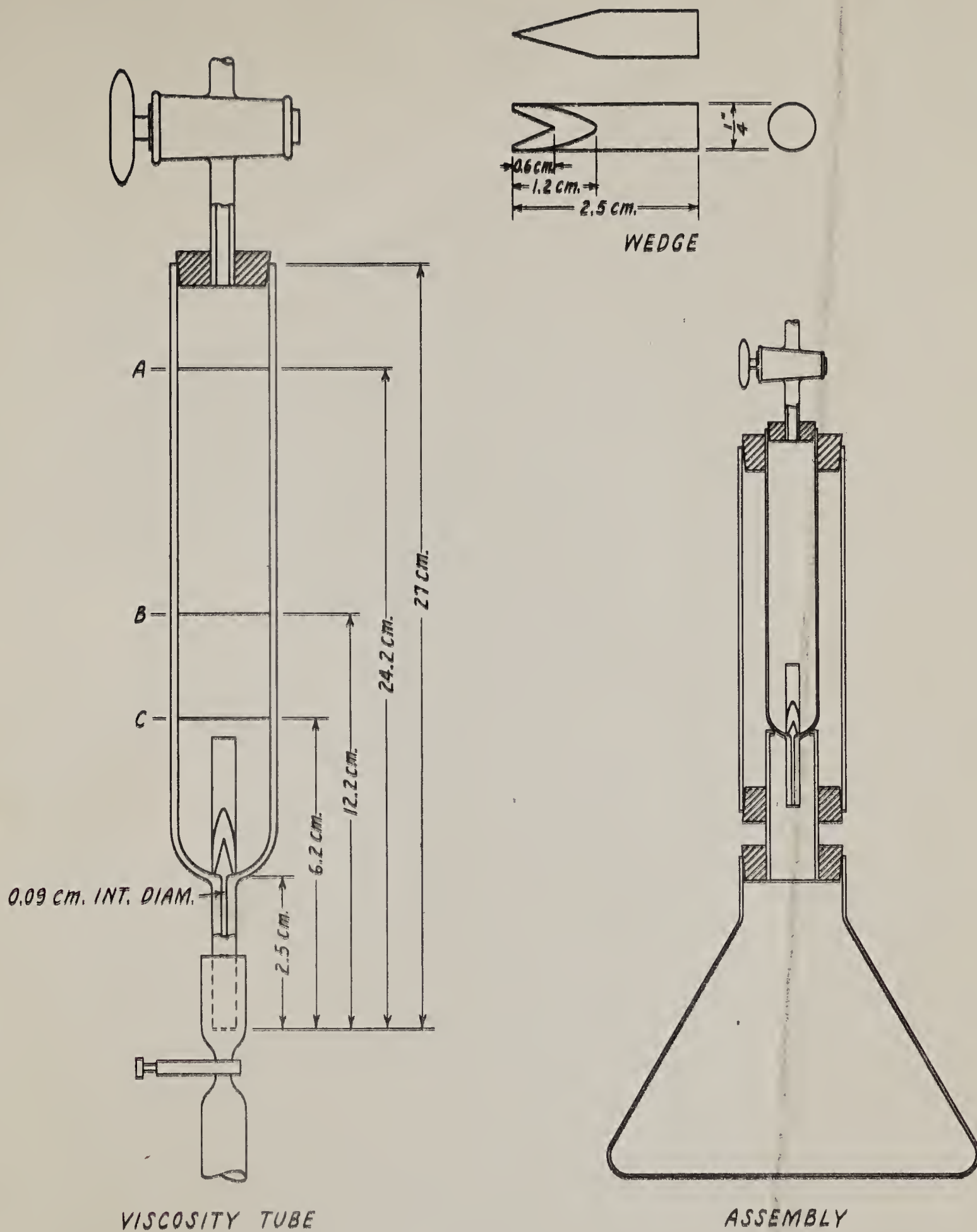


FIG. 5—APPARATUS FOR THE DETERMINATION
OF CUPRAMMONIUM VISCOSITY OF PULP

